Structure of the "Structureless" Replica Film for Electron Microscopy

By Shigeto YAMAGUCHI

(Received August 8, 1951)

Introduction

The thin films, which reprint faithfully the elevations and depressions of the surfaces of substances, are called "structureless" replica in electron microscopy. It is known that the oxide replica[1] and electrodeposited films[2] formed on metal surfaces give more resolved images than Formvar replica. It has been demonstrated in the present study that the structureless oxide replica has a crystallographic structure distinguishable from that of Formvar or collodium replica. The reason why the oxide, sulphide and electrodeposited replica films give the resolved images in electron microscopy are to be explained in the present study.

Experimental

The specimen of iron single crystal used here was a piece of wire (diameter, 2 mm.; length, 10 mm.). This was etched with C_2H_5OH-Br (10:1 by vol.) solution for 10-30 seconds. The oxide replica was formed on this etched surface by the author's method[3] and it was stripped from the substrate by Mahla-Nielsen's method[4]. The micrograph of this replica film is shown in Fig. 2. In Fig. 2 there are octahedral crystals oriented parallel to each other and the (001) planes of these crystals are inclined by 25-30° to the replica film. The electron diffraction pattern from the etched surface of the specimen showed the same inclination of (001) plane to the macroscopic surface as that in microscopic observation. This coincidence verified the faithfulness of the oxide reprint performed here.

The electron beam running perpendicular to the replica film of Fig. 2 gave the diffraction pattern of Fig. 1, which verified the existence of regularly oriented Fe_3O_4 crystals. The oxide crystals formed on metal single crystals orientate themselves according to the orientation of the substrate[5]. On the contrary, Formvar replica gives the diffraction pattern consisting of diffuse haloes. The orientation of the oxide particles formed on the boundary plane (*e. g.*, (111) plane in Fig. 2) of single crystal should be distinguishable from the orientation of oxide particles of another face (*e. g.*, $(\bar{1}11)$ plane in Fig. 2). Therefore, the diffraction spots obtained from the oxide replica appear in the separated positions on a back focal plane of objective lens, which are determined by the orientation of the oxide particles to the incident beam (*vid.* Fig. 3).

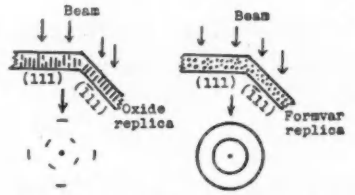

Fig. 3.—The diffraction pattern of oriented oxide replica and that of Formvar replica.

Discussion

The diffraction pattern obtained on a focal plane of a microscope behaves as a new diffraction lattice for the observable image (Abbe's principle); as a matter of fact, this was demonstrated with the electron microscope in three stages[6]. It is, therefore, reasonable that the sharp diffraction spots obtained from oxide replica on a focal plane lead to more resolved images than Formvar replica giving diffuse haloes.

According to the diffraction experiment, the oxide particles formed on the polycrystalline

(1) "Metallurgical Application of Electron Microscope" Monograph and Report Series No. 8, Institute of Metals, London, 1950.

(2) R. Weil and H. J. Read, *J. Appl. Phys.*, **21**, 1068 (1950); G. M. Corney, *J. Appl. Phys.*, **22**, 682 (1951).

(3) S. Yamaguchi, *J. Appl. Phys.*, **22**, 680 (1951).

(4) E. M. Mahla and N. A. Nielsen, *J. Appl. Phys.*, **19**, 378 (1948).

(5) H. R. Nelson, *J. Chem. Phys.*, **5**, 252 (1937).

(6) A. C. van Dorsten, H. Nieuwdorp and A. Verhoeff, *Philips Tech. Rev.*, **12**, 33 (1950); M. E. Haine, P. S. Page and R. G. Garfitt, *J. Appl. Phys.*, **21**, 173 (1950).

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metals are arranged at random. The orientation of the oxide particles to their substrate can be recognized with the oxidized surface of a single crystal, as is shown in Fig. 2. It is, therefore, plausible that the small oxide particles formed on the individual crystals of polycrystalline metal surface orientate themselves in a small area. This fact makes it possible that the oxide replica gives a resolved image and is suitable for dark-field illumination in microscopy. The same results as for the oxide replica should be applicable to the electrodeposited films on metal surfaces.

It is impossible for silver to obtain oxide replica film for microscopy. This metal gives the stable sulfide film on its surface, which is formed with sodium sulfide solution and can be stripped off the substrate with nitric acid. This sulfide film gave a more resolved image (Fig. 4) in the present study than Formvar replica. It is concluded here that the films on metals formed chemically give more resolved images than Formvar replica of metal surface mechanically prepared.

Summary

The reason the oxide replica gives a more resolved image in electron microscopy than Formvar or collodium replica is because the small oxide particles (50-100 Å.) composing replica film are oriented according to the orientation of the metal crystals of substrates. The electrodeposited replica and sulphide film formed on metals give the resolved images in microscopy. This is explained in the same way as for oxide replica.

Prof. N. Kameyama, Prof. S. Mizushima and Mr. K. Sakatani (director of Scientific Research Institute Ltd.) have constantly given the author encouragement in persuing this study, and his thanks are extended to them.

Scientific Research Institute, Ltd.,
31 Kamifujimae Komagome, Bunkyo-ku, Tokyo

New Method of Preparation of Reduced Strychnine Reagent for the Nitrate Determination in Seawater

By Yoshihiro MATIDA

(Received February 28, 1951)

The determination of nitrate is the essential work in the oceano-chemical studies. Since H. W. Harvey[1] applied the G. Deniges's reduced strychnine method[2] to the colorimetric determination of nitrate in sea water, this reagent has been used universally in such studies.[3] The writer has reported with regard to the Harvey's method applied to his oceano-chemical studies of Tokyo Bay.[4] As the Harvey's method of preparation presents some trouble and inconvenience, he has devised a newly preparing reduced strychnine reagent by the use of liquid amalgam.

Inconvenient points of Harvey's method are as follows: (1) The time of reduction is so long as from several hours to more than twenty hours. (2) The extent of the reduction is not constant every time. (3) Zinc of high purity is necessary. Even if amalgamation of zinc is perfect, iron and lead are occasionally dissolved and on account of these impurities this reagent shows pink color even in the absence of nitrite or nitrate in the sample water. (4) Zinc is unnecessarily consumed in mere hydrogen generation. (5) When concentrated sulfuric acid is added after the reduction, a large quantity of zinc sulfate crystallizes out and also the generation of heat and hydrogen chloride is so violent that the operation is very troublesome. (6) Reduced strychnine is oxidized by oxygen or nitric oxide in the atmosphere.

The application of liquid amalgam to analytical chemistry was made by Prof. M. Kobayashi.[6] Of the excellent characteristics of

(1) H. W. Harvey, *J. Mar. Biol. Assoc., N. S.*, **14**, 71-88 (1926).
(2) G. Deniges, *Bull. soc. chim.*, **9**, 544-546 (1911).
(3) D. Rehford, *Commonwealth of Australia, Council for Scientific and Industrial-Research, Bull.*, No. 220 (1947).
(4) Y. Matida, in press.
(5) Y. Miyake, "Water Analysis," Tokyo, 1949, p. 102.
(6) K. Nakazono, *J. Chem. Soc. Japan*, **42**, 526 (1921).

this application, the following points[7] are worthy of special notice: (1) Reduction velocity is accelerated by shaking. (2) Wasteful consumption of zinc is avoided. (3) By the substitution of the air in the reductor with suitable inactive gas (carbon dioxide is the most convenient) the reoxidation of reduced strychnine is avoided.

Experiment and Discussion

I. Operation.—(1) Method of reduction. Into the reductor (Fig. 1) the acid solution of

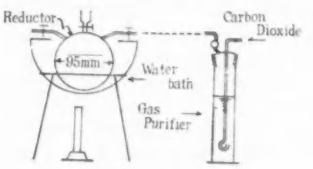


Fig. 1.

strychnine sulfate (0.27 g./20 cc.) and 150 g. liquid amalgam were added, then carbon dioxide was vigorously passed from Kipp's apparatus. The reductor was heated on a water-bath for three minutes. Hereafter it was heated and shaken for two and three minutes respectively. When the sum of shaking periods attained to the definite time, zinc amalgam was taken out into a beaker, carbon dioxide having been passed slowly through the reductor. Then 120 cc. of concentrated sulfuric acid was added and thoroughly mixed.

The purpose of passing carbon dioxide is to protect the reduced strychnine from reoxidation by the oxygen in the atmosphere as D. Rochford's indication, and also by this operation the contamination due to nitrate or nitrite in the laboratory air is preserved.

(2) Colorimetry. In a small test tube with glass-stopper, 5 cc. of sample water or standard solution was taken, then about 0.2 g. of purified sodium chloride or two drops of concentrated hydrchloric acid were added. After the dissolution of sodium chloride, 5 cc. of the reagent were slowly poured on the sample water along the inner side of the tube. After stirring, the tube was preserved in a dark and cold place for definite time. The extinction coefficient of the colored solution was determined with the Pulfrich's photometer or compared with the standard color solution (aqueous solution of safranine red was used). The usefulness of the addition of chloride ion is already found[8] and the writer recognized that the above mentioned quantity of sodium chloride was necessary and sufficient.

II. Preriminary Experiment.—In the first place the suitable acid and its concentration for reduction were studied. From the results, 9 *N* sulfuric acid solution was adopted.

III. Criticism on Shaking Period, Reserving Time and Reproducibility by the Method of Variance Analysis.—The difference of color developing power due to change in shaking period and preserving time was tested. Also the reproducibility—whether two reagents prepared by strictly identical procedure have the same color developing power or not—was investigated. Simaltaneously by this factorial analysis the interrelations of these factors were tested.

Table 1*

	D1		D2	
	H1	H2	H1	H2
B1	1.7, 2.3	2.8, 1.1	−0.6, −0.7	0.8, 3.2
B2	0.2, 1.4	0.0, 0.4	2.0, 1.7	0.2, 1.3
Sum	1.9, 3.7	2.8, 1.5	1.4, 1.0	1.0, 4.5

	D3		Sum
	H1	H2	
B1	0.4, −1.0	2.8, 3.5	16.3
B2	−0.6, −0.5	0.1, 3.1	9.3
Sum	−0.2, −1.5	2.9, 6.6	25.6

D: Reduction time (D1···24 minutes, D2···18 minutes, D3···12 minutes).
H: Preserved time (H1···Immediately after reduction, H2···after 30 days).
B: Repetition ··· B1 and B2 were prepared strictly by the same method.

* The values of this table were obtained as follows. The colored solution (NO_3-N 500 microgram/1.) was compared with safranine red solution (0.005 %), then the constant value deduced from the observed value.

Table 2

Factor	Variance	Dregree of freedom	Mean square
D	0.36	2	0.18
H	7.48	1	7.48*
B	2.04	1	2.04
DH	9.61	2	4.81*
HB	4.79	1	4.79*
BD	4.71	2	2.36
DBH	3.24	2	1.62
R(DHB)	11.59	12	0.97
DHBR	43.82	23	

(7) S. Isimaru, "Experimental Studying Method of Chemistry" Analytical Chemistry, **2** (1942), Tokyo.
(8) B. M. G. Zuwicker and P. J. Robinson, *J. Mar. Res.*, **5**, 214 (1944).

In Table 1, the results of the experiment are shown. Table 2 is the results of variance analysis, in which the mark (*) shows that the factor is significant when the level of significance is 0.05. From this analysis the following conclusions have been obtained: (1) Color developing power changed in preservation. (2) The interrelation of shaking period and reproducibility, and also that of preservation and reproducibility were recognized.

VI. Characteristics of this New Reagent. — (1) Absorption Curve. The curve observed with the Pulfrich's photometer is shown in Fig. 2. From this result the filter S 53 is adopted for the colorimetric determination of nitrate in sea water. Also it was recognised that the aqueous solution of safranine red, used as an artificial standard by L. H. N. Cooper,[9] can be used.

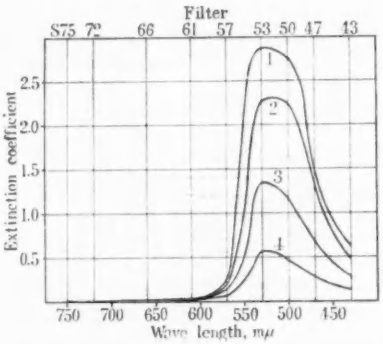


Fig. 2.—Absorption curves of the colored solutions produced by the reactions of reduced strychnine reagents and aqueous solutions of nitrate: curve 1, the product of the new reagent and the aqueous solution containing 200 γ/1. nitrate nitrogen; curve 2, 0.005% aqueous solution of safranine red; curve 3, the product of Harvey's reagent and the aqueous solution containing 200 γ/1. nitrate nitrogen; curve 4, the product of the new reagent and the aqueous solution containing 50 γ/1. nitrate nitrogen.

(2) The Time for Developing the Maximum Intensity of Coloration. After the addition of the reagent, the time for developing the maximum coloration differed with the change in the nitrate concentration. But, twelve hours' standing is enough for any concentration (Fig. 3). The colored substance was easily decomposed by the action of light, so the colorimetric observation needs rapid operation and much care should be taken to protect the colored solution from the light.

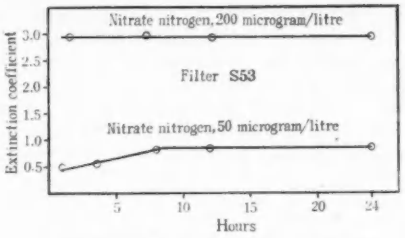


Fig. 3.—A figure to show the time of color development.

(3) The Relation Between the Extinction Coefficient and the Concentration of Nitrate Nitrogen. Ordinarily in natural sea water, nitrate nitrogen concentration is about 500 microgram per litre or less. So in Fig. 4 the calibration curve between extinction coefficient and nitrate nitrogen concentration is shown in this range.

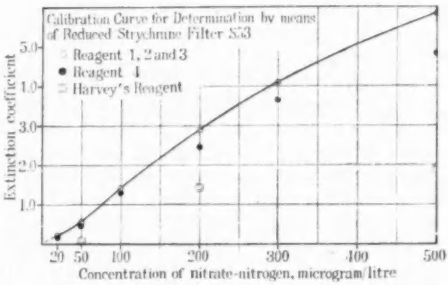


Fig. 4.—A figure to show the relation between the extinction coefficient and the concentration of nitrate. The reduction times to prepare the reagent 1, 2, 3 and 4 are 24, 18 12 and 5 minutes respectively.

(4) Application to Sea Water. To portions of sea water, various quantities of nitrate were added, then the concentrations thereof in the waters were determined. The results were additive, so there might be no considerable salt error larger than the experimental error. Nitrate nitrogen shows the same color, so the correction of this salt was made as follows: In the first place the corresponding extinction coefficient of the nitrite, obtained from the calibration curve thereof (Fig. 5), was subtracted from the measured extinction coefficient of the sample. Nitrite was determined by the use of Griess-Romijn's reagent.

(5) Sensitiveness of the New Reagent. The

(9) L. H. N. Cooper, *J. Mar. Biol. Assoc., N. S.*, **18**, 161 (1932).

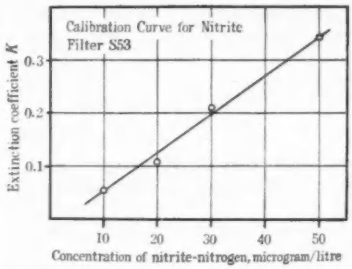


Fig. 5.—A figure to show the relation between the extinction coefficient and the concentration of nitrite.

concentration of this reagent is 1.93 g. per litre as strychnine sulfate. In B. M. G. Zuwicker's report 6 milli-molar strychnidine solution (1.92 g./1.) showed the extinction coefficient 3.48 in the presence of 280 microgram nitrate nitrogen per litre. The new reagent's extinction coefficient in the same concentration of nitrate nitrogen was higher than 3.8, so the new reagent and Zuwicker's one may be of nearly equal sensitiveness. Harvey's reagent aged thoroughly showed considerably lower value than the new one as shown in the fourth figure.

Cooper reported that 0.0008 per cent safranine red solution equaled nitrate nitrogen from 90 to 130 microgram. Also Rochford's reagent showed that 0.0025 per cent solution of the dye equaled 100 or 200 microgram of the nitrate nitrogen. The writer's showed the following relation: 0.005 per cent safranine red solution equaled 150 microgram nitrate nitrogen per litre. So the new reagent is considered to be an excellent one.

Conclusion

Preparation of the Reagent.—(1) 4 g. strychnine sulfate were dissolved in 150 cc. of 18 *N* sulfuric acid. (2) Into the reductor 10 cc. of the strychnine solution, 10 cc. of water and 150 g. liquid amalgam were added. Then the strychnine was reduced for 15 minutes by the method stated above. (3) After the reduction 120 cc. concentrated sulfuric acid were added and they were preserved in a glass bottle of good quality, cleaned with bromine water. It was better to let it stand in a dark and cool place.

Convenient Points of this Method.—(1) The time of preparation is shortened. (2) Reproducibility of the reagent is enhanced. (3) Zinc of high purity is not necessary. (4) Wasteful consumption of zinc is avoided completely, so the operation of adding sulfuric acid is very easy. (5) There is no need of aging. (6) By the replacement of the air in the reductor with carbon dioxide the reoxidation of the reduced strychnine is avoided.

The writer wishes to express his hearty thanks to Prof. H. Goto for his valuable criticisms and desires to acknowledge the helpful suggestions given by Mr. K. Tanii throughout the investigation. He also wishes to thank Mr. S. Tanaka for the suggestions concerning statistical treatment of the results.

Freshwater Fisheries Laboratory Fisheries Agency Tsukishima, Chuō-ku, Tokyo.

Research on Activation Energy. II. Some Applications of the Empirical Rule

By Sanshiro KUME and Kiyoteru OTOZAI

(Received May 18, 1951)

Introduction

One of the authors has previously proposed a new empirical rule for the calculation of the activation energy and shown that the rule holds well for triatomic and tetratomic reactions.[1] The present report concerns further applications of the rule for the more complicated reactions. If we denote the distance

(1) K. Otozai, this Bulletin, **24**, 218 (1951). Details will be published in the Scientific Papers from Osaka University.

corresponding to the inflexion point on the potential-energy curve or to the maximum point on the attractive force curve between two atoms "*the activated internuclear distance*" and the bond, which appears only in the activated complex "*the activated bond*," the present rule can be expressed as follows: among all the possible structures, which can be constructed by the use of the fixed values of the activated internuclear distances of the bonds to be broken as well as to be formed, such a structure, in which the sum of the energies of the activated bonds becomes minimum, represents the structure of the activated complex and this minimum sum of the energies of the activated bonds gives the activation energy of the reaction, when it proceeds in the exothermic direction.

Thus for the tetratomic reaction of the type:

the bonds to be broken are X–Y and W–Z, those to be formed are X–W and Y–Z and the activated bonds, which appear only in the activated complex, are X···Z and Y···W. Hence according to the present rule, among all the possible structures, which can be constructed by the use of the fixed values of the activated distances r^*_{XY}, r^*_{YZ}, r^*_{ZW}, and r^*_{WX}, such a structure, in which the sum of the energies of the activated bonds X···Z and Y···W becomes minimum, represents the structure of the activated complex, and this minimum sum of the energies gives the activation energy of the reaction, when it proceeds in the exothermic direction.

As the potential-energy function $U(r)$, which is necessary to carry out the calculations according to the present rule, Rydberg's equation:[2]

$$U(r) = -D_e\{a(r-r_e)+1\}e^{-a(r-r_e)}$$

is adopted, where D_e represents the equilibrium dissociation energy, and r_e represents the equilibrium internuclear distance. And the constant a, which is characteristic of the pair of atoms, can be calculated by means of the equation:

$$a = 9.28\times10^{-3}\times\omega_e\sqrt{\mu/D_e} = 38.3\times\sqrt{k_0/D_e},$$

where ω_e is the frequency of vibration (cm.$^{-1}$), μ the reduced mass per mole, and k_0 the force constant (megadyne/cm.). So it can readily be shown that the activated distance r^* is given by the equation:

$$r^* = r_e + 1/a.$$

(2) R. Rydberg, *Z. Phys.*, **73**, 381 (1932).

Addition of Hydrogen and Halogen to Ethylene

The addition reaction of hydrogen or halogen to ethylene:

can be treated by means of the present method, if one of the double bonds of ethylene is assumed to be independent of the reaction. The data necessary for the calculation are tabulated in Table 1, where D_e of C—·—C bond was assumed as the difference between that of C═C and C——C, r^* of C—·—C bond the arithmetical mean of the internuclear distance of C═C and C——C, and r_e of C–Cl, C–Br and C–I the sum of the covalent radii of respective atoms.

Table 1

Fundamental Data Necessary for the Calculation for the Addition of Hydrogen and Halogen to Ethylene

Bond	$D=D_e$, kcal.	r_e, Å.	ω_e, cm.$^{-1}$	μ	a, Å.$^{-1}$	r^*, Å.
C . . C	41					1.44
Cl–Cl[3]	57					2.32
Br–Br[3]	46					2.64
I–I[3]	36					3.04
C–Cl	66.5[4]	1.76	712[5]	8.95	2.42	2.19
C–Br	54.0[4]	1.91	603[5]	10.42	2.46	2.32
C–I	45.5[4]	2.10	534[5]	10.96	2.44	2.51
H–H[3]	103					1.12
C–H	87[4] / 80[6]	1.09[7]	2988[8]	0.923	2.86 / 2.98	1.44 / 1.43

The results of the calculation are given in Table 2 and compared with the observed values as well as those calculated by the semi-empirical method of Eyring. From Table 2

(3) *Cf.* the preceeding paper.

(4) L. Pauling, "The Nature of Chemical Bonds," Cornell University Press, New York, 1940, p. 53.

(5) R. A. Ogg, Jr., and M. Polanyi, *Trans. Faraday Soc.*, **31**, 604 (1935).

(6) H. Sponer, "Molekülspektren und ihre Anwendungen auf chemische Probleme," Julius Springer, Berlin, 1935.

(7) L. Pauling, "The Nature of Chemical Bonds," p. 168.

(8) I. Nitta, "The Structure of the Molecule," Tokyo, 1942, p. 126.

Table 2

Activation Energies for the Addiiion of Hydrogen and Halogen to Ethylene

Reaction	Activation energy: Addition obs.	Addition i	Addition ii	Reverse reaction obs.	Reverse reaction i	Reverse reaction ii
$CH_2{:}CH_2+H_2=CH_3{\cdot}CH_3+30$	43	54.8 (46.4) [10]	43 (48) [11]	—	84.8 (62.4) [10]	—
$CH_2{:}CH_2+Cl_2=CH_2Cl{\cdot}CH_2Cl+36$	—	34.8	25.2	—	70.8	80.4
$CH_2{:}CH_2+Br_2=CH_2Br{\cdot}CH_2Br+21$	(30) [9]	31.0	24.4	—	52.0	50.2
$CH_2{:}CH_2+I_2=CH_2I{\cdot}CH_2I+15$	—	20.2	22.4	(36) [9]	35.2	30.0

i. According to the present method.
ii. According to the semi-empirical method of Eyring.

we can see that the present rule holds well for the addition of halogen but somewhat unsatisfactorily for the addition of hydrogen, while just the reverse is the case for the semi-empirical method of Eyring. But it may be worth noting to point out that the difference between the observed and calculated values according to the present method for the addition of hydrogen is remarkably reduced if $D_e = 80$ kcal. is used for the C–H bond as is shown in the table.

Atomic Reactions involving Sodium and Halogen Atoms

Since the bond between sodium and halogen atoms can not be expressed in the usual manner by a single potential-energy curve, the present method can not be applied for the reaction involving these atoms without any additional assumptions. Polanyi *et al.*[12] have previously calculated the activation energies of the reactions of the sodium atom with methyl and phenyl halogenides by constructing the so-called potential-energy profile. But according to Eyring *et al.*[13] these calculated values may be in error, because no allowance is made for the resonance at the activated state.

If we assume for the reaction:

$$Na\cdot + X\cdot\cdot Y \rightarrow \begin{matrix} & X^- & \\ Na^+ & \cdots\cdots & Y \end{matrix} \rightarrow Na^+X^- + \cdot Y$$

the energy of the activated bond $Na^+\cdots Y$ in the same way as for the bond $Na\cdots Y$, we can apply the present rule for this type of reaction, where X denotes halogen and Y the hydrogen atom etc. The data necessary for the calculation are tabulated in Table 3, where D_e

Table 3

Fundamental Data Necessary for the Calculation for the Reactions Involving Sodium and Halogen Atoms

Bond	$D=D_e$, kcal.	r_e, Å.	ω_e, cm.$^{-1}$	μ	a, Å.$^{-1}$	r^*, Å.
Na^+Cl^-	98[15]					2.88
Na^+Br^-	88[15]					3.03
Na^+I^-	72[15]					3.26
H–Cl[16]	102					1.65
H–Br[16]	87					1.80
H–I[16]	71					2.05
Na–H	44	1.88[6]	1170.8[6]	0.96	1.60	2.50
C–Cl[17]	67					2.17
C–Br[17]	54					2.32
C–I[17]	46					2.51
Na–C	33	2.31			1.63	2.92
Cl–Cl[16]	57					2.32
Br–Br[16]	46					2.64
I–I[16]	36					3.04
Na–Cl	32	2.53			1.60	3.16
Na–Br	28	2.68			1.64	3.29
Na–I	25	2.87			1.68	3.47

of Na–H, Na–C, Na–Cl, Na–Br and Na–I were calculated as a geometrical mean of Na–Na and H–H, C–C, Cl–Cl, Br–Br and I–I respectively, r_e of Na–C, Na–Cl, Na–Br and Na–I as the sum of covalent radii of respective atoms, and a of Na–Br as the arithmetical mean of

(9) Somewhat uncertain.
(10) D_e=80 kcal. was used.
(11) ρ=10% was used, while for all the other cases ρ=14%.
(12) R. A. Ogg and M. Polanyi, *Trans. Faraday Soc.*, **31**, 1375 (1935); M. G. Evans and E. Warhurst, *ibid.*, **35**, 593 (1939).
(13) G. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Company, New York and London, 1941, p. 322.
(14) L. Pauling, *ibid.*, p. 338.
(15) R. G. Pearson, *J. Chem. Phys.*, **17**, 969 (1949).
(16) *Cf.* preceding report.
(17) *Cf.* Table 1.

Na–Cl and Na–I. The activated distance r^* of Na^+Cl^-, Na^+Br^- and Na^+I^- was calculated by means of the equation:

$$r^* = 1.04 \times (r_{Na^+} + r_{X^-}),$$

derived as the distance corresponding to the inflexion point on the potential-energy curve of Na^+X^- given by Pauling:[14]

$$U(r) = 331 \times \{-1/r + 296 \times 10^{-4} \times (r_{Na^+} + r_{X^-})^8/r^9\},$$

where r_{Na^+} and r_{X^-} are the so-called standard radii of sodium and halogen ions respectively. The force constant k_0 for Na–C, Na–Cl and Na–I, which is necessary for the computation of a by means of the above-mentioned equation:

$$a = 38.3 \times \sqrt{k_0/D_e},$$

was calculated according to the empirical rule of Badger:[18]

$$k_0 = c_{ij}/(r_e - \delta_{ij})^3,$$

where c_{ij} and δ_{ij} are the constants dependent on the rows of the periodic table containing the two atoms.

The results of the calculation for some reactions involving sodium and halogen atoms are tabulated in Table 4 and compared with the experimental results. The observed values enclosed in brackets are the mean for several reactions with varying sorts of organic halides. From Table 4 it may be said that the present rule holds equally well for the reactions involving the heteropolar bonds under the appropriate assumptions as for the ordinary reactions.

Table 4

Activation Energies for the Atomic Reactions Involving Sodium and Halogen Atoms

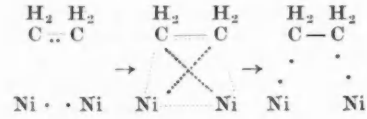
Reaction	Activation energy	
	obs.	calc.
$Na\cdot + Cl\cdot\cdot H \rightarrow Na^+Cl^- + \cdot H - 4$	6	7.3
$Na\cdot + Br\cdot\cdot H \rightarrow Na^+Br^- + \cdot H + 1$	0	2.2
$Na\cdot + I\cdot\cdot H \rightarrow Na^+I^- + \cdot H + 1$	0	1.2
$Na\cdot + Cl\cdot\cdot CR \rightarrow Na^+Cl^- + \cdot CR + 31$	(5.5)	2.1
$Na\cdot + Br\cdot\cdot CR \rightarrow Na^+Br^- + \cdot CR + 34$	(3.0)	1.4
$Na\cdot + I\cdot\cdot CR \rightarrow Na^+I^- + \cdot CR + 26$	(1.2)	0.8
$Na\cdot + Cl\cdot\cdot Cl \rightarrow Na^+Cl^- + \cdot Cl + 41$	0	2.4
$Na\cdot + Br\cdot\cdot Br \rightarrow Na^+Br^- + \cdot Br + 42$	0	1.2
$Na\cdot + I\cdot\cdot I \rightarrow Na^+I^- + \cdot I + 36$	0	0.5

(18) R. M. Badger, *J. Chem. Phys.*, **2**, 128 (1934); *ibid.*, **3**, 710 (1935).

Adsorption of Hydrogen and Ethylene on Nickel

Since the dissociative adsorption of hydrogen on Nickel:

and the so-called associative adsorption of ethylene on Nickel:



are important processes relating to the heterogeneous catalytic reactions, we have applied the present rule for these processes. The data used for the calculation are tabulated in Table 5, where the data for H–H and C..C are the same as in Table 1, and the constant a of Ni–C was computed by means of Badger's rule. The result of the calculation are given in Table 6 and graphically shown in Fig. 1, together with the results of the calculations by other authors. The values of the Ni–Ni distance given in the second column of Table 6 are chosen, taking into consideration the actual structure of the nickel crystal surface as is shown in Fig. 2, where the radii of the two circles, *i. e.*, 4.98 Å. and 6.02 Å. represent the length of the linear form of the activated complexes:

Table 5

Fundamental Data Used for the Calculation of the Adsorption on Nickel

Bond	$D = D_e$, kcal.	r_e, Å.	ω_e, cm.$^{-1}$	μ	a, Å.$^{-1}$	r^*, Å.
H–H	103					1.12
Ni–H	60[19]	1.48[19]	1900[19]	0.983	2.25	1.93
C..C	41					1.44
Ni–C	38[20]	1.92[21]			2.74	2.29

(19) G. Okamoto, J. Horiuchi and K. Hirota, *Scient. Papers Inst. Phys. Chem. Res. Tokyo*, **29**, 223 (1936).
(20) J. Horiuchi, *Catalyst*, **2**, 1 (1947).
(21) A. Sherman, C. E. Sun and H. Eyring, *J. Chem. Phys.*, **3**, 49 (1935).

$$\underset{\text{Ni}}{\overset{\leftarrow 1.93\rightarrow}{\cdots\cdots}}\underset{\text{H}}{\overset{\leftarrow 1.12\rightarrow}{\cdots\cdots}}\underset{\text{H}}{\overset{\leftarrow 1.93\rightarrow}{\cdots\cdots}}\underset{\text{Ni}}{\overset{\leftarrow\!\!\!

Research on Activation Energy. III. On Activation Energy for the Adsorption of Hydrogen on Reduced Copper

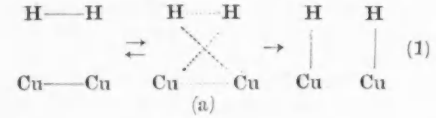
By Sanshiro KUME and Kiyoteru OTOZAI

(Received June 12, 1951)

Introduction

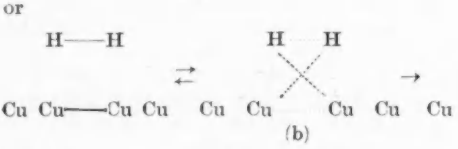
Because of experimental difficulties most of the hitherto observed values of the activation energy for the adsorption of hydrogen on metals are not fully reliable. T. Kwan[1] has recently obtained, however, the reliable value for the activation energy of the adsorption of hydrogen on reduced copper, since in this case the velocity of adsorption has a moderate value. So we intend to calculate the activation energy for this process by means of the empirical rule which we have previously proposed,[2] as a typical example of the heterogeneous reaction.

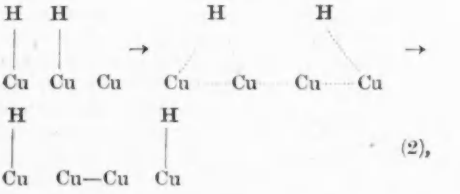
In order to calculate the activation energy for a reaction we must have clear knowledge of the mechanism of the given reaction. Since the velocity of the adsorption of hydrogen on reduced copper was found by the experiment of Kwan[1] to be the first order with respect to hydrogen, the mechanism of the reaction must be either



(1)

or





(2),

if we assume the hydrogen molecule to be adsorbed dissociatively.[3] So long as no information is given on the adsorption isotherm, it is not possible to decide which of the above given mechanisms is the correct one. But if it is assumed that the configuration of the activated complex (a) of the mechanism (1) and that (b) of the mechanism (2) are the same, the activation energy must be the same for both mechanisms. The activation energy for the reaction has been calculated under this assumption, and compared with the observed value of Kwan.

Calculation of Activation Energy

The method of the calculation refers to the previous paper.[2] The fundamental data used for the calculation are given in Table 1, where

Table 1

Fundamental Data Used for the Calculation

Bond	D_e(kcal./mole)	r_e(Å.)	ω_e(cm.$^{-1}$)
H—H	109.2[4]	0.75[4]	4276[4]
Cu—H	62.2[5]	1.46[4]	1940.1[4]

D_e is the equlibrium dissociation energy, r_e the internuclear distance and ω_e the frequency of the vibration of the given bond.

If we calculate the activated distance r^*, the distance between two atoms in the actived state, for H-H and Cu-H from the data given in Table 1 by the use of the equations[2]

$$r^* = r_e + 1/a$$

$$a = 9.28 \times 10^{-3} \omega_e \sqrt{\mu / D_e},$$

we obtain $r^* = 1.12$ Å. and $a = 2.68$ Å.$^{-1}$ for H-H and $r^* = 1.90$ Å. and $a = 2.27$ Å.$^{-1}$ for Cu-H. But since the activated distance has a fixed

(1) T. Kwan, *J. Research Inst. Catalysis (Hokkaido Univ.)*, **1**, 95(1949); T. Kwan, This Bulletin, **23**, 73 (1950).

(2) K. Otozai, This Bulletin, **24**, 218(1951); K. Otozai, *Collected Papers from the Faculty of Science, Osaka Univ.*, No. 20; S. Kume and K. Otozai, This Bulletin, **24**, 257(1951).

(3) G. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Company, New York and London, 1941, p. 356.

(4) H. Sponer, "Molekülspektren und ihre Anwendungen auf chemische Probleme," Julius Springer, Berlin, 1935. D_e (109.2 kcal.) is sum of the ordinary dissociation energy (103 kcal.) and the zero point energy (6.2 kcal.).

(5) A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules," Chapman and Hall, London, 1947. In the calculation of D_e the zero point energy was neglected in view of the uncertainty of the spetroscopic value itself.

value for the respective sort of bond, the maximum possible distance between Cu-Cu for which the dissociative adsorption of hydrogen can occur, must be equal to the total length, *i. e.*, 4.92 Å., of the linear or stretched form of the activated complex:

$$\underset{\longleftarrow\!\!\!

rule is ± 3 kcal. and the estimation of the fundamental data may contain some errors. The above obtained conclusion that hydrogen can be adsorbed more easily on the surfaces (110) and (111) than (100) of copper crystal has not yet been experimentally ascertained. But it may be worth pointing out the fact that according to the experiment of Leidheiser and Gwathmey[7] the catalytic reaction between hydrogen and oxygen takes place more quickly on the surface (111) than on the surface (100) of copper.

(7) H. Leidheiser, Jr., and A. T. Gwathmey, *J. Am. Chem., Soc.*, **70**, 1200, 1206 (1948)); H. Leidheiser, Jr, and A. R. Meelheim, *ibid.*, **71**, 1122 (1949).

Summary

The activation energy for the activated adsorption of hydrogen on copper metal has been calculated by the use of the empirical rule previously proposed. The calculated value 19.4 kcal./mole agrees very well with the observed value 20 kcal./mole of T. Kwan. It has been concluded that hydrogen will be adsorbed more quickly on the surfaces (110) and (111) than on the surface (100) of copper crystal.

The authors wish to express their sincere thanks to Prof. T. Titani for his interest in this research.

Faculty of Science, Osaka University, Osaka

Statistical Thermodynamics of Solution of Rigid Rod-like Molecules

By Tōru KAWAI

(Received June 13, 1951)

Introduction

Recent theories of polymer solutions may be classified into two types, namely, the one based on the lattice model which was developed by Flory,[1] Huggins,[2] and others, and the other represented by Zimm's treatment[3] formally equivalent to that of imperfect gas theory. These two, however, include many questions to be discussed. The former involves a somewhat paradoxical situation in the separate evaluation of the entropy and energy terms in the partial molal free energy expression, although the success of the semi-empirical free energy expression justifies considerable confidence being placed in its application to thermodynamic properties of polymer solutions. Namely the statistical configurations of polymer molecules in solution must be influenced by the energetical interaction between polymer and solvent, and the heat of dilution must be determined by these configurations. The latter is more reasonable on this point, but often its calculation is not so easy as applicable to the practical cases. Furthermore, polymer-solvent interaction is not taken up explicitly, although the "average force potential" between segments involves it implicitly.

Now in the case of rigid large molecules circumstances are extremely simplified because the cofigurations are not affected by the energetical interaction. Thus the separate evaluation of the energy and entropy terms will be possible in this case. From this point of view, the above two methods were discussed in the present paper in relation to the most simple model for rigid rod-like molecules.

(1) P. J. Flory, *J. Chem. Phys.*, **10**, 51 (1942); **9**, 660 (1941).
(2) M. L. Huggins, *J. Chem. Phys.*, **9**, 440(1941); *J. Phys. Chem.*, **46**, 151 (1942).
(3) B. H. Zimm, *J. Chem. Phys.*, **14**, 164 (1946).

Discussion of Zimm's Result

In spite of its great simplicity, the theory of solution of rigid rod-like molecules has not been presented except by Zimm, who obtained the following result[3]

$$A_2 = \pi N_0 d l^2 / 4M^2, \qquad (1)$$

where A_2[4] is the second coefficient in the

(4) The A_2 values characterize the most important deviation from Raoult's law.

equation expressing osmotic pressure as power series in concentration analogous to the virial expression for gases, N_0 Avogadro's number, d the diameter, l the length, and M the molecular weight of the rod-like molecules. Employing the relationship $\pi d^2 l/4 = M/N_0\rho$, Eq. (1) reduces to

$$A_2 = 1/\rho^2(\pi/4)d^3N_0, \qquad (2)$$

where ρ is density of the solute. This result shows that Eq. (1) is not adequate in distinguishing th enature of actual polymer-solvent systems, since A_2 is a function of only ρ and d, and these values will not differ so much for various cellulose derivatives which are supposed to be rod-like molecules.(5)

In recent theories osmotic pressure expression involves one or two parameters which were introduced through some approximate treatments. These parameters are insufficient to account for experimental data or are not of theoretical significance (for example, the well used μ is merely an empirical one characterizing a given system). Actually, the partial molal free energy of dilution is a function of size and shape of solvent and solute molecules (spacial factors) and energetical interaction between solvent and solute. But even if the above factors were introduced in the osmotic pressure expression through amplification and refinement of the existing theory, we cannot compare them with osmotic data without estimating some of these factors in some other way. It may be said, however, that the approximate treatments in current theories must be improved by knowledge of the actual polymer. Now it must be noted that Zimm's treatment (the "rigid body approximation" for large molecules) is obviously an approximation applicable only to the case of long rigid rod-like molecules suspended in an effectively continuous and structureless solvent. Thus the effect of the above spacial factors on the entropy term must be investigated theoretically as well as experimentally. For this purpose, we adopted a lattice model consistent with the information obtained from the molecular constructions of solute and solvent.

Eq. (2) may be written

$$A_2 = \{V_1/(\pi/4)d^3N_0\}/V_1\rho^2 = \frac{1}{2}\{(V_1/N_0)/(\pi/8)d^3\}/V_1\rho^2 \qquad (3)$$

where V_1 is molal volume of solvent. Thus Zimm's result coincides with Flory's[1], based on lattice model as seen in his first paper on polymer solutions, when the volume of the segment equals $(\pi/8)d^3$. It is interesting that

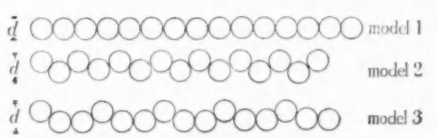


Fig. 1.—Hypothetical model of long rigid rod-like molecules.

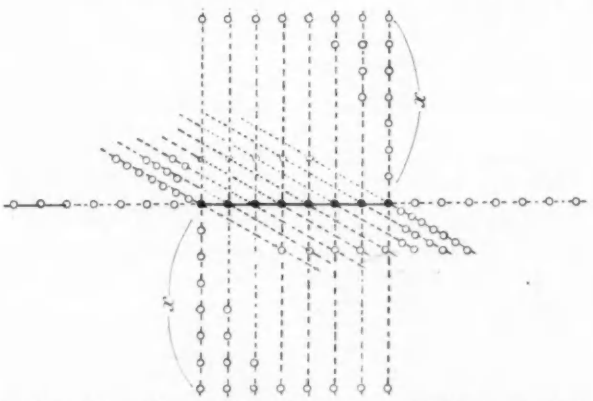


Fig. 2.—Illustration of the region v (cubiclattice): •–•–•–• indicates the first molecule A_1.

(5) It is supposed from the information on viscosity and light scattering etc., that the molecules of cellulose derivatives are not entirely rigid rods, but are somewhat flexible especially when they are long. Our procedure may also be applicable to such cases if the effect of energetical interaction on configurations of polymer molecules can be neglected, since it involves little bending of successive submolecules (See Fig. 1).

this volume equals that of the submolecule assumed in the following section.

New Treatment of Solution of Rigid Rod-like Molecules

Let us consider a hypothetical model of the

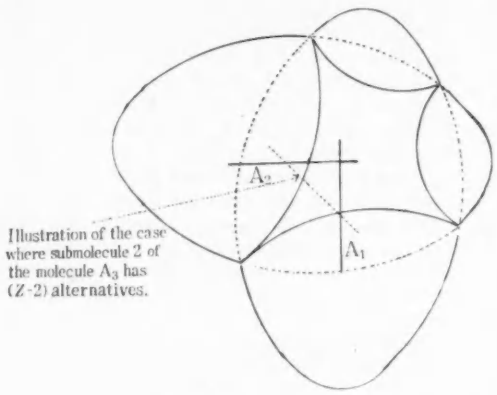


Illustration of the case where submolecule 2 of the molecule A_3 has $(Z-2)$ alternatives.

Fig. 3.—Illustration of the rigion v'.

rod-like molecules consisting of x spherical submolecules as illustrated in Fig. 1. For model 1 the volume of the submolecule is $\pi(d/2)^3$ and agrees with that mentioned above. The following procedure may be allowed for models 2, 3, etc.,[5] although somewhat different values must be adopted for the volume of the submolecule.[5] Now we assume N_0 lattice sites throughout the solution and make the above submolecule correspond to one lattice site. The type of lattice must be determined by the relative position of the submolecules in solution (accordingly by coordination number z). The solute molecules are first added one at a time, then the solvent molecules, counting the number of different ways setting each molecule in the lattice sites one after another in order to obtain the total number of configurations.

Submolecule 1 of molecule A_1 (the first solute molecule) can be placed in any of N_0 sites. Submolecule 2 of this molecule has a number of alternatives, z, equal to the coordination number. The position of the molecule A_1 is fixed when that of its first two submolecules is, because the successive submolecules must be connected linearly.[5] Thus the number of the configuration for the molecule A_1 is zN_0. Next, the second molecule A_2 is added. Here we consider linearly connected x sites starting from each submolecule of the first molecule for all coordinations in the circumference of the molecule, as illustrated in Fig. 2. The total number of these sites is given by[6]

$$v=(z-2)(x-1)x+3x-2\doteqdot(z-2)x^2-(z-5)x. \quad (4)$$

When submolecule 1 of the molecule A_2 is added in these sites, the number of configurations for the molecule A_2 is $v(z-1)$.[7] When it is added in other (N_0-v) sites, the number of configurations is $(N_0-v)z$.

Similarly for the third molecule A_3, we may write $(N_0-v')z+(v'-2x)(z-1)^*$ when the molecule A_2 was added in the above v sites, and $(N_0-2v)z+2(v-x)(z-1)$ when it was added in other (N_0-v) sites. Here the meaning of v' may be seen from Fig. 3, and $(z-1)^*$ is not strictly equal to $(z-1)$, although the difference between them is negligibly small.[8]

Proceeding in this manner to the N-th solute molecule, making the product of corresponding factors, and summing up all of them, a great number of terms are obtained. When concentration of solute is very small, these terms can be arranged as follows, assuming that the terms containing more than two of $(v-x)$ or $(v'-2x)$ etc. may be neglected, and that $v'\doteqdot 2v$[9]:

$$\begin{aligned}
&N_0(N_0-v)(N_0-2v)\cdots\{N_0-(N-1)v\}z^N\\
&+[N_0(N_0-v)\cdots\{N_0(N-2)v\}(N-1)(v-x)\\
&+N_0(N_0-v)\cdots(N-2)(v-x)\{N_0-(N-1)v\}\\
&+N_0(v-x)(N_0-2v)\cdots\\
&\qquad\{N_0-(N-1)v\}]z^{N-1}(z-1)\\
&=z^N\{N_0(N_0-v)\cdots[N_0-(N-1)v]\}\times\\
&\quad[1+(v-x)/(N_0-v)\times(z-1)/z+\cdots\\
&(N-1)(v-x)/[N_0-(N-1)v]\times(z-1)/z] \quad (5)
\end{aligned}$$

Thus the total number of configurations for N solute molecules is given by[10]

$$W=z^N/2^N N!\times\{N_0(N_0-v)\cdots[N_0-(N-1)v]\}\times\{1+(v-x)/(N_0-v)\times(z-1)/z+\cdots$$

(6) The v values given by Eq. (4) are a little larger than what we need, owing to overlapping of some of the v sites in a certain type of lattice, but are approximately available to such cases. One of the most simple cases where Eq. (4) holds strictly (cubic lattice) is illustrated in Fig. 2.

(7) The second molecule overlaps with the first in any one of x linearly connected sites starting from submolecule 1 of the second molecule A_2 for one coordination of it.

(8) When one of certain sites on the plane containing the previously added two molecules with in the range v' is occupied by submolecule 1 of the molecule A_3, the number of alternatives of its second submolecule is $Z-2$, but the number of these sites are very small in this range (see Fig. 3).

(9) Obviously from Fig. 3, this approximation is unsatisfactory, but the calculation is tedious and it is almost hopeless to think of getting results without employing it.

(10) This procedure is formally equivalent to Ichimura's on dilute solutions of coiled polymer (*J. Phys. Soc. Japan*, **3**, 308 (1948)).

$$\times(N-1)(v-x)/[N_0-(N-1)v]\times(z-1)/z\} \quad (6)^{(11)}$$

$$\fallingdotseq z^N/2^N N!\times(N_0/v)!/(N_0/v-N)!\times\{1+(z-1)/z\times N^2/2N_0\times(v-x-2vxN/3N_0)\}, \quad (6')$$

where the value 2 is the symmetrical number. Here N_0 is replaced by its equivalent $n+xN$ and n is regarded as the number of solvent molecules when each of them equals the submolecule in size and shape. After addition of all the solute molecules, the remaining sites are filled with the solvent molecules. This introduces no increase in the number of distinguishable configurations. Introducing the relationship $\Delta S/R=\ln W$ and replacing factorial terms with Stirling's approximation, the entropy of the system is obtained. Then, deriving the entropy of mixing by the usual manner and differentiating it with respect to n, the partial molal entropy becomes

$$\begin{aligned}\Delta\bar{S}_1 &= R\{1/v\times\ln[1-vN/(n+xN)] \\ &\quad -(z-1)/2z\times(v-x)[N/(n+xN)]^2 \\ &\quad +vx(z-1)/6z\times[N/(n+xN)^3+\cdots\cdots\} \\ &= R\{v_2^2/x+[v/2x^2-(z-1)/2z \\ &\quad \times(v-x)/x^2]v_2^2+\cdots\cdots\}, \end{aligned} \quad (7)$$

where $v_2=xN/(n+xN)=$ volume fraction of solute.

In our case, formulation of the energy term is simplified because we can evaluate it apart from the configurations of the system. Thus the heat of mixing may be written[12]

$$\Delta H=K(z-2)xNv_2, \quad (8)$$

where $K=\varepsilon_{12}-(\varepsilon_{11}+\varepsilon_{22})/2$.

Or $$\Delta\bar{H}_1=K(z-2)v_2^2=\alpha v_2^2 \quad (9)$$

(these notations are similar to those employed usually).

Combining Eq. (9) with Eq. (7), there is obtained for partial molal free energy

$$\Delta\bar{F}_1=\Delta\bar{H}_1-T\Delta\bar{S}_1=-RT\{v_2/x+[v/2x^2-(z-1)/2z\times(v-x)/x^2-\alpha/RT]v_2^2\}. \quad (10)$$

Hence, according to the definition of A_2,

$$\begin{aligned}A_2 &= 1/V_1\rho^2\times\{v/zx^2+(1-1/z)/x-\alpha/RT\} \\ &= 1/V_1\rho^2\times\{(z-2)/2z+(z-3-2/z)/2x \\ &\quad -\alpha/RT\}\fallingdotseq 1/V_1\rho^2(1/2-1/z-\alpha/RT). \end{aligned} \quad (11)^{(13)}$$

This result coincides with that of Huggins, who derived it on solution of coiled molecules. However, it is possible to point out that the coordination number, z, holds its original significance explicitly in our case, since such approximation averaging the "distribution density" as used by Huggins is not adopted here.

Next, we adopted an approximate method introduing the effect of size and shape of solvent on the viewpoint that Flory's modification[1] for the entropy expression owing to the volume ratio β of segment for solvent may be unsatisfactory and that the spacial factors should be considered in more detail. When the above submolecule is a times larger than the solvent molecule, we assume conventionally a lattice sites in each submolecule, taking the coordination number, z', determined by the spacial factors of the solvent.

As mentioned above, the operation of packing the solvent molecules which equal in size and shape the submolecule in the remaining sites is exactly equivalent to that of setting solute molecules in the sites without considering the existence of solvent molecules. Therefore, the total number of different configurations W'' in this case will be obtained from W', which is substituted by aN_0 for N_0, an for n, and axN for xN, in the above expression for W, multiplying by a factor due to the fact that a solvent molecules must be in a group in the new lattice sites. Hence

$$W''=W'W_1\Big/\binom{aN_0}{an}, \quad (12)$$

where W_1 is the number of different ways in which n molecules, each occupying a sites, can be packed in aN_0 sites without overlapping. Affording a good approximation for small and spherical molecules, W_1 was evaluated by Osawa as follows[14]:

$$W_1=\left\{\binom{N_0}{n}z'^N\right\}^a\Big/\binom{z'N_0}{n}^{a-1} \quad (13)$$

Entropy of this system is obtained in the

(11) The terms in the latter bracket in Eq. (6) are arranged as seen here, employing the relations: $(N-1)(v-x)/[N_0-(N-1)v]\fallingdotseq(N-1)\times v/N_0-(N-1)\times n/N_0\times[1+(N-1)v/N_0]$, $(v/N_0\ll1,\ n/N_0\ll1)$; $1+2+\cdots\cdots+(N-1)=N(N-1)/2$; $1^2+2^2+3^2+\cdots\cdots+N^2=N(N+1)\times(2N+1)/6$.

(12) This result is the same as that for coiled molecules, since the number of polymer-solvent pairs are expressed as seen here in all cases.

(13) Perhaps employing another procedure, Zimm obtained a similar result (J. H. Hildebrand and R. L. Scott "The Solubility of Non-electrolytes," Reinfold Publishing Corp., New York, 1950.

(14) F. Osawa, *Busseiron Kenkyu*, **8**, 10 (1947).

same manner as mentioned previously. Differentiating the entropy of mixing with respect to an, there is obtained for the partial molal entropy:

$$\Delta\bar{S}_1'' = \Delta\bar{S}_1 + R\{(a-1)/a \times \ln(1-v_2) + (z'-1)\ln(1+v_2/(z'-1))\} \quad (14)$$

$$= R\{v_2/x + [1/2 - 1/z - (a-1)/2a + (a-1)/a(z'-1)]v_2^2 + \cdots\}. \quad (14')$$

Hence,

$$A_2 = 1/V_1\rho^2 \times [1/2a - 1/z + (a-1)/a(z'-1) - \alpha/RT]. \quad (15)$$

This procedure may detect the effect of size and shape of solvent on the entropy term approximately, although strictly speaking it can be reasonable only when the types of the above two lattices are one and same ($z=z'$). When $z=z'$, $z \gg 1$, Eq. (15) reduces to

$$A_2 \simeq 1/V_1\rho^2 \times (1/2a - 1/az - \alpha/RT). \quad (16)$$

Eq. (16) corresponds to Flory's modification for Eq. (11). The values of entropy terms in Eq. (15) and (16) are estimated for cellulose derivatives-various solvents systems, assuming $z=z'=12$(closely compacted)and that the volume of the submolecule $=\pi d^3/8 \fallingdotseq 1000$ Å.^{3}($d \fallingdotseq 7$ Å.)[15]. These values are shown in Table 1, being

Table 1

Estimation of Values of the Entropy Term for Various Solvents

Solvent	a	$1/2a-1/az$	$1/2a-1/z+(a-1)/a(z'-1)$	$1/2a$
Acetone	8.22	0.050	0.058	0.061
Methyl acetate	7.59	0.055	0.062	0.066
Ethyl acetate	6.17	0.068	0.074	0.081
Butyl acetate	4.63	0.091	0.096	0.108
Cyclo-hexanone	5.76	0.072	0.079	0.087
Dioxan	7.07	0.059	0.066	0.071
Chloroform	7.51	0.056	0.063	0.067

compared with the values of $1/2a$. Obviously from our assumption, this procedure is concerned only with dilute solutions. At high concentrations, Flory's result[1] $\Delta\bar{S}_1 = v_2/x + 1/2a \times v_2^2 + \cdots$ in his early papers may be also applicable to our case. As is shown in the preceding section, Zimm's result corresponds to Flory's approximation, if we assume the "segment" as mentioned above. In the commonly used range of concentrations, the true value of A_2 is supposed to be a little greater than that calculated by Eq. (15) owing to the terms neglected in Eq. (5).

Now the well-used parameter μ is usually expressed by the form $\beta+\alpha/RT$. Regarding the correlation of the value of β with molecular details of polymer solutions, Zimm[16] has shown that β would have a value of 0.49 for long rigid rods. When the effect of the size of the solvent is not considered, the value 0.49 for β corresponds to $z \fallingdotseq 2.0$, showing that the relation $\beta=1/z$ is not available to practical cases. On the other hand, our procedure anticipates values of β in the range 0.40~0.44, depending principally on the values of a. The exact values to be assigned to a, however, cannot be deduced theoretically because of the difficulty of bridging the gap between the actual polymer in solution on one hand and the idealized model composed of submolecules arranged in the hypothetical lattice on the other. Namely, the difficulty in our estimation of the entropy terms lies in the estimation of the size of the above submolecule. It is supposed, however, that the values of β estimated here may be rather appropriate from Zimm's evaluation in Hildebrand's book quoted in the footnote (13), although we cannot know his procedure in detail.

Many osmotic data for samples selected systematically and the facts from other physicochemical measurements will enable us to estimate the entropy and energy terms respectively. As is shown in Table 1, the contribution of the entropy of dilution to A_2 will not differ so much for the systems of cellulose derivatives and various solvents, and especially if more data were available to the systems, in a series of solvents for a given polymer, we could estimate

Table 2

Comparison with Experiments

System	Temp., °C.	$A_2V_1\rho^2$ entropy	A_2entropy $\times 10^4$(calc.)	$A_2\times 10^4$ (exper.)
Nitrocellulose in acetone	20	0.054	4.13	10.89
	40			10.23
Nitrocellulose in methyl acetate	20	0.062	3.35	11.97
	40			11.17
Nitrocellulose in ethyl acetate	20	0.074	3.23	11.68
	40			10.07
Nitrocellulose in butyl acetate	20	0.096	3.15	7.85
	40			7.32

(15) From our knowledge of viscosity, and light scattering etc. d is supposed to be in the range of 8~15Å.

(16) B. H. Zimm, Am. Chem. Soc. Meeting, Sept. 1947. (P. Doty, M. Brownstein and W. Schleuer, *J. Phys. Coll. Chem.*, **53**, 213 (1949)).

the energy term and solvent power from them. In Table 2, the A_2 values calculated from our experiment[17] on nitrocellulose (N content 10.5 %) are compared with those evaluated above.[18] Table 2 shows that acetone, methyl acetate, and ethyl acetate are alike better solvents than butyl acetate.

Summary

(1) A new thermodynamic relationship applicable to dilute solution of rigid rod-like molecules was derived, employing a lattice model.

(2) Small deviation from Zimm's result for rigid rod was discussed here, considering the effect of size and shape of solvent and solute.

(3) Although quantitative discussion is impossible because of the difficulty of the estimation of the size of the submolecule, it may be said that the contribution of entropy of dilution to A_2 (the second virial coefficient in osmotic pressure expression as power series in concentration) will be less for rigid rod-like molecules than for coiled molecules, and furthermore, the difference between such systems as cellulose derivatives in a series of solvents will be very small.

The author wishes to thank his director K. Makishima for constant encouragement and many helpful suggestions. This report was presented at the Fourth Meeting of the Chem. Soc. Japan, at Tokyo University, April, 1951.

Laboratory of Textile Chimistry, Tokyo Institute of Technology, Tokyo

(17) K. Ishikawa and T. Kawai, paper read at the Fourth Meeting of Chem. Soc. Japan, April, 1951.

(18) The usual relations, $\Delta S_1=(V_1\pi-V_1'\pi')/(T-T')$ and $\Delta H_1=(V_1\pi/T-V_1'\pi'/T')/(1/T-1/T')$, often give the values of ΔS_1 and ΔH_1 with error as great as 100—200%.

Studies on Foams. VII. Theory of Foam Formation of Dyestuff Solution

By Masayuki NAKAGAKI

(Received July 23, 1951)

In the preceding paper[1] the close relation between the foam formation and the work required to remove the unit area of adsorption layer, U_f, has been found for alcohol solutions and electrolyte solutions. The theory will be extended, in the present paper, to dyestuff solutions. The calculation of the work U_f was based, in the preceding paper, upon the observed data of the surface tension, but it is, now, replaced by a molecular kinetic theory.

Let the energy required to remove one mole of solute from the adsorption layer to the bulk solution be U_0, and the concentration of solute in the solution and in the layer be C and C_f (mole/cc.), respectively. U_0 is such as an adsorption potential. The velocity of desorption, G_d (mole/cm.^{2}/sec.), that is the moles of molecule passing through the unit area in the unit time from the adsorption layer to the bulk solution is calculated as follows. If the velocity distribution of solute molecules in the adsorption layer obeys to Maxwell-Boltzmann's distribution law, the velocity component in x direction, that is the direction normal to the surface, is in the average,

$$\overline{v_x(0)}=2\sqrt{\frac{kT}{2\pi m}} \qquad (1)$$

If a molecule goes and returns between the upper and lower boundaries of adsorption layer, of thickness d (cm.), with the velocity $\overline{v_x(0)}$, the frequency $\bar{\nu}_0$ is, since the path in one period is $2d$,

$$\bar{\nu}_0=\frac{\overline{v_x(0)}}{2d}=\frac{1}{d}\sqrt{\frac{kT}{2\pi m}} \qquad (2)$$

This is analogous to the well known equation in the statistical mechanics of liquid. As for liquid, two models are often used as the first approximations: "smooth potential model" and "harmonic oscillator model". Free volume

(1) M. Nakagaki, This Bulletin, **23**, 127 (1950).

per molecule v in the smoothed potential model and the frequency of molecule ν in harmonic oscillator model are related with each other by the equation[2]:—

$$\nu=\frac{1}{v^{1/3}}\sqrt{\frac{kT}{2\pi m}}\,. \tag{3}$$

Eq. (2) is the one dimensional analogue of Eq. (3). From this point of view, it will be permitted to apply the kinetic theory of gas to the adsorption layer.

The average x-component velocity of molecules, having the kinetic energy greater than U_0/N_0, is,

$$v_x(U_0)=\frac{kT}{A(U_0)}\exp\left(-U_0/RT\right) \tag{4}$$

where

$$A(U_0)=\int_{\sqrt{(2/m)(U_0/N_0)}}^{\infty}\exp(-mv_x^2/2kT)\mathrm{d}v_x \tag{5}$$

and N_0 is Avogadro's number. Therefore, from Eq. (2),

$$\bar{\nu}=\frac{v_x(U_0)}{2d}=\frac{kT}{2dA(U_0)}\exp\left(-\frac{U_0}{RT}\right) \tag{6}$$

Let the moles of solute contained in the unit area of the adsorption layer be n_0, and the moles of solute molecule having the kinetic energy greater than U_0 be n, then

$$n/n_0=2A(U_0)/\sqrt{2\pi mkT} \tag{7}$$

and

$$n_0=d\cdot C_\Gamma \tag{8}$$

Therefore:

$$n=2dA(U_0)C_\Gamma/\sqrt{2\pi mkT} \tag{9}$$

If all the molecules, colliding to the boundary between the adsorption layer and the bulk solution with the kinetic energy greater than U_0, desorb, then the rate of desorption G_d is,

$$G_d=n\bar{\nu}=C_\Gamma\sqrt{kT/2\pi m}\exp\left(-U_0/RT\right) \tag{10}$$

Then, calculate the adsorption velocity. Let the saturation amount of adsorption per unit area be N_a (mole/cm.^{2}), the actually adsorbed amount be $\Gamma_2^{(1)}$, and the area already occupied be $\Gamma_2^{(1)}/N_a$. Among the molecules colliding to the surface already occupied, α is assumed to be adsorbed and $(1-\alpha)$ be repelled, and all molecules colliding to the the empty surface $(1-\Gamma_2^{(1)}/N_a)$ is assumed to be adsorbed. The total number of molecules colliding to the surface is $(C/2)\overline{v_x(0)}=C\sqrt{kT/2\pi m}$, so the rate of adsorption G_a, that is the moles of solute adsorbed in unit time per unit area, is

$$G_a=\left\{\left(1-\frac{\Gamma_2^{(1)}}{N_a}\right)+\alpha\frac{\Gamma_2^{(1)}}{N_a}\right\}\cdot C\sqrt{\frac{kT}{2\pi m}} \tag{11}$$

In dynamic equilibrium,

$$G_a=G_a \tag{12}$$

The volume of the adsorption layer per unit area is N_aV_2, where V_2 is the mole volume of solute. Then,

$$C_\Gamma=\Gamma_2^{(1)}/N_aV_2 \tag{13}$$

Therefore,

$$\Gamma_2^{(1)}=\frac{N_akC}{1+(1-\alpha)kC} \tag{14}$$

where

$$k=V_2\exp\left(U_0/RT\right) \tag{15}$$

or

$$\frac{C_\Gamma}{C}=\frac{1}{1+(1-\alpha)kC}\exp\left(\frac{U_0}{RT}\right) \tag{16}$$

When the adsorbed molecules occupy definit sites on the adsorption surface, the molecules colliding to the area already occupied are all repelled, that is $\alpha=0$. Then Eq. (14) becomes:—

$$\text{when}\quad \alpha=0,\quad \Gamma_2^{(1)}=\frac{N_akC}{1+kC} \tag{17}$$

This agrees with Langmuir's equation. When the adsorbed molecule moves freely on the surface and the collision diameter of the molecule is not great, all the molecules colliding to the adsorption surface are thought to be adsorbed. In this case, $\alpha=1$, Eq. (16) becomes:

$$\text{when}\quad \alpha=1,\quad C_\Gamma/C=\exp\left(U_0/RT\right) \tag{18}$$

which is in agreement with Boltzmann's equation used in the preceding paper,[1] for alcohol solutions.

Eq. (16) is rewritten as:

$$\left.\begin{aligned} &C_\Gamma/C=\exp\left(U_1/RT\right)\\ &\text{where}\quad U_1=U_0-RT\ln\{1+(1-\alpha)kC\}\end{aligned}\right\} \tag{19}$$

U_1 is the energy required to remove one mole of solute from the adsorption layer to the bulk solution. $R\ln\{1+(1-\alpha)kC\}$ is the entropy corresponding to the assumption that, $(1-\alpha)$ of molecules colliding to the surface are repelled. This gives the impression as if the transposition of molecule from the adsorption layer to the bulk solution is easier in the case when the repelling is present. In the case of triphenylmethane dyes, the molecules are considered as plates of about 4 Å. in thickness and 200 Å.^{2} in area, and the adsorbed molecules

(2) R. H. Fowler and E. A. Guggenheim: "Statistical Thermodynamics", Cambridge, 1939, p. 324.

are lying parallel to the liquid surface. Almost all molecules colliding to the "already occupied area" are, therefore, repelled, and α is assumed nearly equal to zero. Eq. (19) then becomes,

$$U_1 = U_0 - RT \ln (1+kC). \qquad (20)$$

Gibbs' equation is, if the activity coefficient of solute is assumed to be equal to unity for the dilute solution,

$$\Gamma_2^{(1)} = -(1/RT)(\partial\sigma/\partial \ln C) \qquad (21)$$

Using this and Langmuir's equation (17), and assuming that k or U_0 is independent to concentration,

$$1-\sigma/\sigma_0 = (N_a RT/\sigma_0) \ln (1+kC) \qquad (22)$$

is obtained. Rewriting the natural logarithms to the common one,

$$1-\sigma/\sigma_0 = A \log (1+kC) \qquad (23)$$

where
$$\left.\begin{aligned} A &= 2.303 \times N_a RT/\sigma_0 \\ k &= V_2 \exp (U_0/RT) \end{aligned}\right\} \qquad (24)$$

Eq. (24) agrees with the results cited in Freundlich's "Kapillarchemie," Vol. 1, p. 84. Eq. (23) is the well known Szyszkowsky's experimental equation, which is recognized as to fit well with many experimental data.

Size of dye molecule is calculated using van der Waals radii cited by Pauling[3]. The area of benzene molecule is calculated as 38.7 Å.^{2}, if C–C distance is assumed to be 1.39 Å., C–H distance 1.07 Å. and van der Waals radius of hydrogen atom 1.2 Å. The area of benzene molecule is calculated as 39.7 Å.^{2}, by the assumption that the density is 0.88, and the thickness is 3.7 Å. These two values of the area of benzene molecule agree well with one another. The radical $(X-C_6H_4-)_3C$ may be called as "triphenyl methane nucleus", (where X is hydrogen or nitrogen atom). The triphenyl methane nucleus is generally thought to have a triangular co-planar structure[4]. The area of it is assumed to be equal to about three times as large as that of benzene, 116 Å.^{2} Radii of hydrogen atom and methyl radical are assumed to be 1.2 Å. and 2.0 Å., respectively. Areas of various radicals calculated as above are cited in Table 1. Areas, S, of some dye ions calculated by the summation of data of Table 1 are shown in Table 2. The thickness of ions are assumed to be equal to that of benzene, or 3.7 Å. The saturated adsorption amount per 1 cm.^{2}, N_a (mole/cm.^{2}), is calculated from the value of area, S, by the equation,

$$N_a = 1/(N_0 S) = 1.66 \times 10^{-24}/S \qquad (25)$$

where N_0 is Avogadro's number. Mole volume of dye ion in the adsorption layer, V_2 (cc./mole), is obtained, assuming the thickness of the adsorption layer being equal to the thickness of ion,

$$V_2 = 3.7 \times 10^{-8}/N_a \qquad (26)$$

The density of it, d, is

$$d = M/V_2 \qquad (27)$$

where M is the formula weight of dye ion. These values are also shown in Table 2. The density data cited are $0.8 \sim 0.9$, which are fairly smaller than the value of solid dye, that is about 1.5, and is rather similar to the value of benzene, 0.88. This is quite plausible, since the molecular interaction in the adsorption layer is fairly weaker than in the crystal state.

Using these values, the coefficient A is calculated from Eq. (24). The value of k is determined so as the experimental values fit the Szyszkowsky's equation (23) best. The value of U_0 is then calculated according to Eq. (24). These are cited in Table 3. In Table 3, E is:

$$E = U_0/SN_0 \qquad (28)$$

Table 1

Areas Occupied by Some Radicals

Triphenyl methane nucleus	$X-C_6H_4-C\begin{matrix}/\\ \\ \backslash\end{matrix}\begin{matrix}C_6H_4-X'\\ \\ C_6H_4-X''\end{matrix}$	116 Å.^{2}
Methyl group	CH_3-	12.5 Å.^{2}
Hydrogen atom	H–	4.5 Å.^{2}
Ethyl group	C_2H_5-	19 Å.^{2}
Benzyl group	$C_6H_5-CH_2-$	45 Å.^{2}
Thickness of molecule (equal to that of benzene)		37 Å.

Table 2

Dimensions of Dye Ions

Dye	Formula weight M	Area of ion S, 10^{-16} cm.^{2}	Saturated adsorption amount N_a, 10^{-10} mole/cm.^{2}	Mole volume V_2, cc./mole	Density d
Methyl violet 5B	448	223.5	0.743	498	0.898
Brilliant green	385	192	0.864	428	0.899
Malachite geeen	329	166	1.000	370	0.889
Crystal violet	372	191	0.868	426	0.873

(3) L. Pauling, "The Nature of the Chemical Bond," New York, 1940, p. 189.

(4) See, *e. g.*, E. Hückel, *Z. Elektrochem.*, **43**, 827 (1937); G. N. Lewis and M. Calvin, *Chem. Rev.*, **25**, 273 (1939).

Table 3

Constants for Adsorption (20°C.)

Dye	A	k, 10^6cc./mole	U_0, 10^{10}erg/mole	E, erg/cm.^{2}
Methyl violet 5B	0.0573	90.4	29.5	21.9
Brilliant green	0.0667	6.1	23.3	20.1
Malachite green	0.0771	2.40	21.4	21.4
Crystal violet	0.0670	1.71	20.2	17.6

It should be noticed that E is nearly equal to 20 erg/cm.^{2} for all dyes.

Using these data, U_1 and $\Gamma_2^{(1)}$ are obtained from Eqs. (20) and (17), respectively. As the product of them:

$$U_F = \Gamma_2^{(1)} U_1 \tag{29}$$

the energy required to remove the unit area of the adsorption layer U_F is calculated. According to the preceding paper[1], U_F should be parallel to the foam formation of the solution. In Fig. 1, calculated values of U_F are plotted along with the foaming ability F

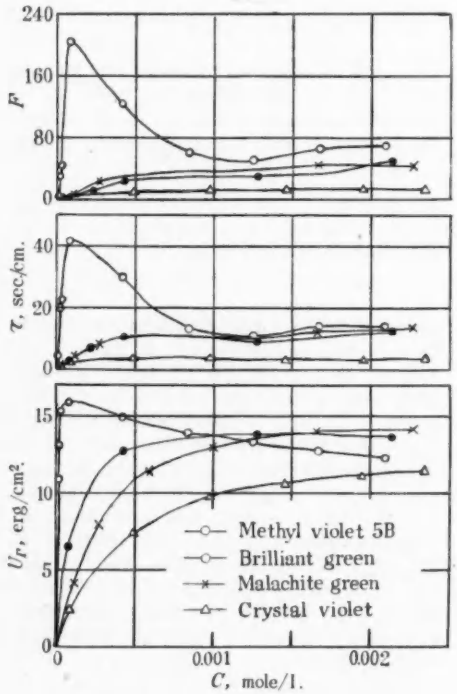


Fig. 1.—The Relation of F and U_F to C.

reported in the third paper of this series.[5] In these triphenyl methane dyes, only methyl violet 5B has a maximum point in its foaming ability-concentration curve. It has been supposed in that paper that this will be due to the enormously large surface activity of this dye. By the calculation in this paper, it is shown that U_F-C curve has a maximum point for methyl violet 5B, while for other dyes no maximum is obtained. The qualitative discussion done in the former paper has been, therefore, justified in this paper.

The fact that E is nearly equal to 20 erg/cm.^{2} suggests an interesting property of the adsorption layer. As described before, the property of the adsorption layer of triphenyl methane dye is somewhat similar to benzene. This is suggested both from its molecular structure and from its density cited in Table 2. Therefore,

$$E \doteqdot u_w + u_{w-0} - u_0 \tag{30}$$

where u_w, and u_0 are internal surface energy of water and benzene, respectively, and u_{w-0} is internal interfacial energy of water-benzene interface. According to International critical Tables,[6]

$$\left.\begin{aligned} u_w &= 118.15 \quad \text{erg/cm.}^2 \\ u_0 &= 67.86 \quad \text{erg/cm.}^2 \\ u_{w-0} &= 52.00 \quad \text{erg/cm.}^2 \end{aligned}\right\} \tag{31}$$

at 20°C. From these data,

$$E \doteqdot 102.3 \quad \text{erg/cm.}^2 \tag{32}$$

is obtained, which is fairly different from the experimental value: $E \simeq 20$ erg/cm.^{2} cited in Table 3. This discrepancy may be ascribed to the fact that the layer of "benzene" is a thin layer of 3.7 Å., so that u_0 and u_{w-0} is different from the value for the bulk of benzene.

Fowler[7] calculated the adhesion energy and obtained

$$E_{1-2}^{adh} = 2\pi \int_0^\infty n_2(j)\mathrm{d}j \int_j^\infty \mathrm{d}f \int_f^\infty n_1(f-j)\,\epsilon_{12}(r) r \mathrm{d}r \tag{33}$$

where E_{1-2}^{adh} is the adhesion energy between phase 1 and phase 2 per unit area, $\epsilon_{12}(r)$ is the interaction energy between molecules distant as r from each other, n_1 and n_2 are the densities of molecules (number of molecules/cc.) in both phases, and j, f, and r are the distances shown in Fig. 2.

For simplicity, it is taken as

(5) M. Nakagaki, This Bulletin, **22**, 200 (1949).
(6) "International Critical Tables", Vol. IV, p. 436.
(7) Fowler, *Proc. Roy. Soc.*, **A 159**, 229 (1937).

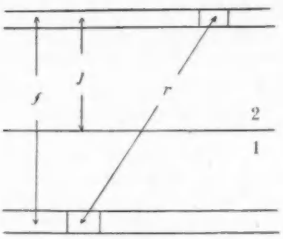


Fig. 2.

$$n_1(f-j)=N_1,\quad n_2(j)=\begin{cases}0 & \text{if } j<R_{12}\\ N_2 & \text{if } j\geqq R_{12}\end{cases}$$
$$\text{and}\qquad \epsilon_{12}=-\mu_{12}/r^6 \qquad (34)$$

where, N_1 and N_2 are constants, showing the density in the bulk of phases 1 and 2, respectively, R_{12} is the sum of radii of molecules 1 and 2, and μ_{12} is a constant. Under these assumption, the equation (33) is simplified as,

$$E_{1-2}^{a/h}=-(\pi/12)N_1N_2\mu_{12}/R_{12}^2 \qquad (35)$$

Then, let u_1, u_2 and u_{12} be the internal surface energy of phases 1, 2, and the internal interfacial energy between phases 1 and 2, respectively. It is obtained that,

$$\begin{aligned}u_1&=-E_{1-1}^{a/h}/2=(\pi/24)N_1^2\mu_{11}/R_{11}^2\\ u_2&=-E_{2-2}^{a/h}/2=(\pi/24)N_2^2\mu_{22}/R_{22}^2 \qquad (36)\\ u_{12}-u_1-u_2&=E_{1-2}^{a/h}=-(\pi/12)N_1N_2\mu_{12}/R_{12}^2\end{aligned}$$

The interfacial energy is sometimes schematicaly explained in a text-book as shown in Fig. 3 a. For a molecule of phase 1, placed at the surface, the lower half of its sphere of action is filled with molecules of phase 1, and

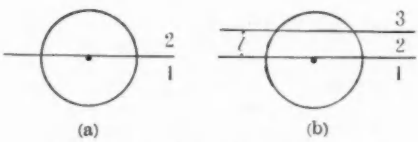


Fig. 3.—A schematic explanation of interfacial energy.

the upper half is filled with molecules of 2, if the thickness of both phases are large enough compared with the radius of the action. The difference of the interactions from two hemispheres causes the interfacial energy between 1 and 2. If, then, the thickness of the layer 2 is smaller than the radius of the sphere, as shown in Fig. 3 b, the interfacial energy between phases 1 and 2 will be different from the ordinary value corresponding to Fig. 3 a. Modifying Fowler's equation (33), the adhesion energy between the bulk phase 1 and the layer 2, thickness of which is l, (Fig. 3 b), is expressed as:

$$\begin{aligned}E_{1-23}^{a/h}=&2\pi N_1\int_0^l n_2(j)\mathrm{d}j\int_j^\infty \mathrm{d}f\int_f^\infty \epsilon_{12}(r)r\mathrm{d}r\\ &+2\pi N_1\int_l^\infty n_3(j)\mathrm{d}j\int_j^\infty \mathrm{d}f\int_f^\infty \epsilon_{13}(r)r\mathrm{d}r\end{aligned} \qquad (37)$$

This is integrated, besides with assumption (34), under the following additional assumption that

$$n_3(j)=N_3,\quad (\text{if } j\geqq l) \text{ and } \epsilon_{13}(r)=-\mu_{13}/r^6 \qquad (38)$$

and obtained that

$$E_{1-23}^{a/h}=-\frac{\pi N_1}{12}\left\{N_2\,\mu_{12}\left(\frac{1}{R_{12(3)}^2}-\frac{1}{l^2}\right)+N_3\mu_{13}\,\frac{1}{l^2}\right\} \qquad (39)$$

As the shortest distance between the centers of gravity of molecule 1 and 2 may be different from the value of R_{12} by the orientation of molecule in the thin layer, it is shown as $R_{12(3)}$. Using Eq. (36),

$$\begin{aligned}E_{1-23}^{a/h}=&(u_{12}-u_1-u_2)\left(\frac{R_{12}^2}{R_{12(3)}^2}-\frac{R_{12}^2}{l^2}\right)\\ &+(u_{13}-u_1-u_3)\,\frac{R_{13}^2}{l^2}\end{aligned} \qquad (40)$$

is obtained.

The energy required to bring a dye molecule (per unit area) from the adsorption layer into the bulk solution, E, is expressed

$$E=-E_{w-w}^{a/h}+E_{w-ow}^{a/h} \qquad (41)$$

In Eqs. (36) and (40), let $1=w$, $2=o$, and $3=w$. Then, under the notice that $u_{ww}=0$, Eq. (41) is rewritten:

$$\begin{aligned}E=&2u_w\left(1-\frac{R_{ww}^2}{l^2}\right)\\ &+(u_{wo}-u_w-u_o)\left(\frac{R_{wo}^2}{R_{wo(w)}^2}-\frac{R_{wo}^2}{l^2}\right)\end{aligned} \qquad (42)$$

If $R_{wo(w)}=R_{wo}$ and $l\gg R_{wo}$, this equation coincides with Eq. (30).

Molecular diameter of water, R_{ww}, is calculated from the density, ρ_w, molecular weight, M_w, and mole volume, V_w, of water and Avogadro's number, N_0,

$$R_{ww}=\frac{1}{\gamma}\left(\frac{V_w}{N_0}\right)^{1/3}=\frac{1}{\gamma}\left(\frac{M_w}{\rho_w N_0}\right)^{1/3} \qquad (43)$$

γ, a constant determined by the molecular arrangement, is assumed rather arbitrarily,

$$\gamma = 0.935, \tag{44}$$

referring to the facts that $\gamma=1$ for simple cubic lattice, $\gamma=0.916$ for the body centered lattice, and $\gamma=0.890$ for the face centered lattice. Then, R_{ww} is calculated as:

$$R_{ww}=3.32\,\text{Å}. \tag{45}$$

For benzene, a similar calculation gives,

$$R_{oo}=5.64\,\text{Å}. \tag{46}$$

and

$$R_{wo}=\left(\frac{R_{ww}+R_{oo}}{2}\right)=4.48\,\text{Å}. \tag{47}$$

It has already been shown by the assumptions in Eq. (34), the boundary surface between phases 1 and 2 is taken as a plane placed on the centers of the phase 1 molecules nearest to phase 2. Then, using the value of the thickness of benzene molecule, δ, or 3.70 Å.,

$$\left.\begin{aligned} R_{wo(w)}&=\frac{1}{2}R_{ww}+\frac{1}{2}\delta=3.51\,\text{Å}.\\ l&=\frac{1}{2}R_{ww}+\delta=5.36\,\text{Å}\end{aligned}\right\} \tag{48}$$

Then, by Eq. (42),

$$E = 21.0\,\text{erg/cm.}^2 \tag{49}$$

is obtained. This agrees well with the values in Table 3, that is $E\simeq 20\,\text{erg/cm.}^2$

Summary

Considering the dynamic equilibrium of adsorption and desorption on the surface of water, Szyszkowsky's equation is derived. Using the area of dye molecule calculated from the molecular structure, U_o and $\Gamma_2^{(1)}$ are estimated to obtain the best conformity with the measurement of the surface tension. U_F calculated by them is compared with the foam formation of these triphenyl methane dyes. Maximum observed in the foaming ability—concentration curve of methyl violet 5 B is explained by its large surface activity. The fact that the energy required to bring the unit area of dye molecule into the bulk solution is about 20 erg/cm.^{2} is justified using the correction of interfacial energy due to the fact that the thickness of the adsorption layer is nearly equal to the dimension of the range of molecular force.

Chemical Institute, Faculty of Science, the University of Tokyo, Tokyo.

Studies on Monomolecular Films. VII. The Effect of Metallic Ions on the Monomolecular Film of Stearic Acid

By Tunetaka SASAKI and Ryôhei MATUURA

(Received August 2, 1951)

Introduction

It is of great importance in the study of monomolecular films of fatty acids on the surface of water to know precisely the effect of ions in the underlying water on the properties of the monolayers. Harkins and Myers[1] noticed that the decrease in the area per molecule of a fatty acid on the surface of alkaline water is chiefly caused by the contamination of divalent ions (especially calcium ion) which make the chains close-packed (20.5 Å.^{2}); in the absence of such ions the molecules may be arranged with their heads close-packed giving approximately the area of 25 Å.^{2}, the area found on dilute acid solutions. Extensive work on the effect of dissolved salts on insoluble monolayers of stearic acid was carried out by Langmuir and Schaefer,[2] who studied

(1) W. D. Harkins and R. J. Myers, *Nature*, **139**, 367 (1937).

(2) I. Langmuir, and V. J. Schaefer, *J. Am. Chem. Soc.*, **59**, 2400 (1937).

in detail the remarkable effect of such metallic ions as calcium, barium and aluminum and proposed a theory of the interaction between ions in the substrate and stearic acid in the film, assuming that the modification of a stearic acid monolayer by the presence of salts is due to the adsorption of salt to the undersurface of the monolayer. It has not been studied systematically, however, how each metallic ion affects the property of a fatty acid monolayer under varying hydrogen ion concentration and, particularly, how the effect can be explained from the standpoint of molecular structure of the resulting metallic soap. Recently studies on metallic soaps have been carried out colloid chemically by many workers and the interesting results have been obtained concerning the structure as well as the colloid chemical properties of metallic soaps.[3],[4],[5] It is the purpose of the present work to investigate the effect of the various metallic ions on the monolayer of stearic acid spread on the surface of the solution of varying hydrogen ion concentration and to discuss the result by taking into consideration the recent studies on metallic soaps as well as the characteristic properties of each metallic ion.

Experimental

The monolayer of stearic acid was prepared from benzene solution on the surface of water containing a salt of concentration of 10^{-4} mol/l.. The salts were used as chloride, nitrate and sulfate. They were purified by the repeated recrystallization. From the preliminary experiment the effect of inorganic anion on the monolayer of stearic acid was found negligible. The tray was made of brass and was coated thickly with paraffin. It was found that, when the surface of the tray was covered thickly with paraffin, the effect of the metallic ions which might come from the tray material on the acid monolayer was not measurable at least in the case where pH of the substrate ranged from 2 to 10. The value of pH of the substrate was controlled by hydrochloric acid and ammonium hydroxide. The use of ordinary buffer salts were particularly avoided since the possibility was considered that the buffer salts might frequently cover the remarkable effect usually encountered in the presence of metallic ions for investigation. The pressuie~area diagram was measured for each monolayer of stearic acid by the method described already.[6]

(3) C. G. McGee, *J. Am. Chem. Soc.*, **71**, 278 (1949).
(4) V. R. Gray and A. E. Alexander, *J. Phys. Coll. Chem.*, **53**, 9, 23 (1949).
(5) R. D. Vold and G. S. Hattiangdi, *Ind. Eng. Chem.*, **41**, 2311 (1949); G. S. Hattiangdi, and M. J. Vold, *ibid.*, **41**, 2320 (1949); etc.
(6) T. Sasaki, *J. Chem. Soc. Japan*, **62**, 796 (1941); R. Matuura and I. Hayasi, *Memoirs of the Faculty of Science, Kyūshū University, Ser. C*, Vol. 1, 31 (1948).

Results

Various metallic ions were examined how they affect the pressure~area curve of the monolayer of stearic acid on the surface of the solution and it was found that they can be classified into two groups according to the difference in the effect. One involves those which cause the monolayer to condense on the alkaline solution and the other those which make it expand in a proper pH range of the solution, characteristic of each metallic ion.

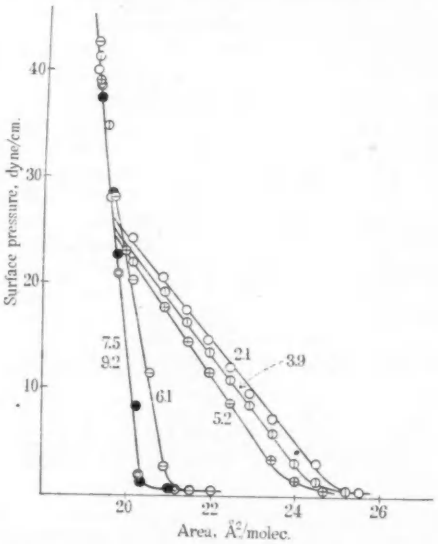


Fig. 1.—Pressure~area curves of the monolayer of stearic acid on water containing calcium ion: The numeral for each curve represents pH of the substrate.

The typical example of the first group is calcium ion. The pressure~area diagram of the monolayer of stearic acid on the surface of water containing calcium ion is shown in Fig. 1. It is obvious from this figure that the effect of calcium ion on the monolayer of stearic acid varies with pH of the substrate. In order to make this relation more distinct, the zero-compression area per molecule of stearic acid is plotted against pH of the substrate as shown by crosses in Fig. 2. The curve shown by small circles in the same figure represents the result of the blank experiment carried out on the surface of water containing no metallic ion. In the absence of metallic ions the monolayer of stearic acid is unstable,

presumably a little soluble, on the alkaline substrate and the area per molecule of stearic acide diminishes sometimes to as small as 15

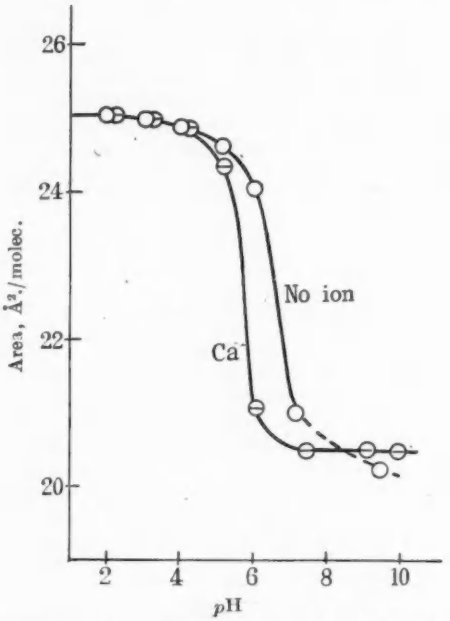


Fig. 2.—Area-*p*H curve of the monolayer of stearic acid on water containing calcium ion.

or 16 Å². On the contrary when calcium ion is present, the monolayer becomes stable enough even on the alkaline substrate to give a definite area of so-called close-packed chain, 20.5 Å². per molecule. On the acid substrate the monolayer of stearic acid is stable irrespective of the presence of calcium ion and gives the area of about 25 Å²., the area of so-called close-packed head. The metallic ions which show the similar effect as calcium ion are barium, magnesium, lead and manganese, but the effect of the last two is rather ambiguous. The pressure~area curve of the monolayer of stearic acid affected by these ions is similar, depending little upon the difference in the nature of these metallic ions.

An example of the second group of metallic ions is aluminum. The pressure~area curve of the monolayer of stearic acid spread on the substrate containing $AlCl_3$ is shown in Fig. 3. It is noticed that aluminum ion remarkably expands the monolayer in a certain range of *p*H, the maximum expansion occurring at *p*H near 7. This is more clearly illustrated in Fig. 4, where the zero-compression area per

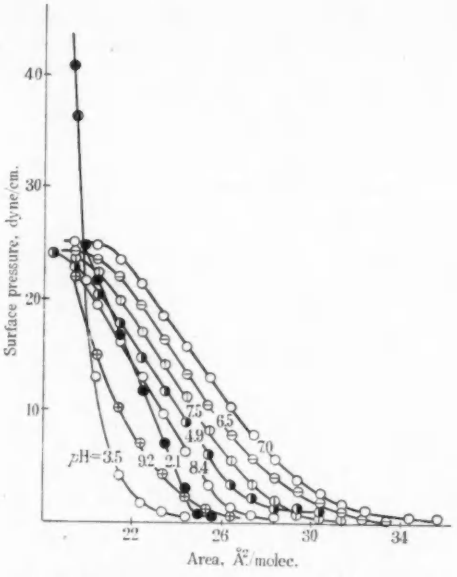


Fig. 3.—Pressure~area curves of the monolayer of stearic acid on water containing aluminum ion.

molecule of stearic acid is plotted against *p*H of the substrate. When *p*H increases beyond the value of maximum expansion, the film becomes gradually unstable. It is noteworthy that the monolayer which is made to expand by aluminum ion has a large compressibility and its collapse pressure is rather small compared with that of the film unaffected by metallic ions, as seen in Fig. 3. In this group of the metallic ions copper, zinc, mercury, cobalt, nickel, iron, cerium and thorium ions are included in addition to aluminum ion. The optimum *p*H of the film expansion is proper for each ion as shown in Fig. 4 in the case of a few metallic ions of this group.

Discussion

It is evident from the experiment of Langmuir and Schaefer[7] that the metallic soap is formed in the film when stearic acid is spread on the surface of water which contains both metallic ions and a suitable amount of hydrogen ion. Hence the remarkable effect of those metallic ions on the monolayer of stearic acid should be discussed from the standpoint of the resulting metallic soaps.

It was shown that ions of the first group, namely calcium, barium and magnesium,

(7) I. Langmuir and V. J. Schaefer, *J. Am. Chem. Soc.*, **58**, 284 (1936).

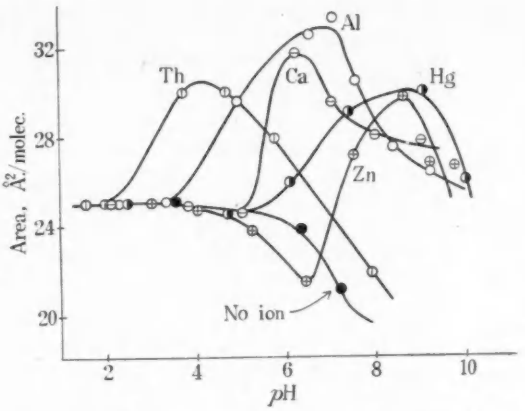
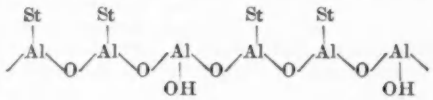


Fig. 4.—Area~pH curves of the monolayer of stearic acid on water containing some metallic ions.

clearly condensed the monolayer of stearic acid on the alkaline solution. This is due to their bivalent bond foining two molecules of stearic acid, thus forming a stoichiometric compound of the type $Me(St)_2$, as has been pointed out by Harkins.[1],[8] This causes the chain close-packed and gives the area of 20.5 Å². per stearate radical, while without these metallic ions the heads are close-packed, giving the corresponding value of 25 Å². Notwithstanding this difference, the structure of the monolayer of these metallic soaps is not essentially different from that of stearic acid, since in both films the long chain molecules are oriented vertically with their nonpolar chains being arranged side by side.

The situation is wholly different in the case of metallic ions of the second group, namely ions of aluminum, thorium, iron, copper, zinc, mercury, cobalt, nickel, etc. The effect of these ions on a stearic acid monolayer causing it to expand and rendering it remarkably compressible suggests that the resulting metallic soap may not be so simple as the soap of calcium, barium and magnesium but may have a rather complicated structure. Since McBain[9] reported for the first time a non-existence of aluminum trisoap, many workers have investigated the properties and structure of aluminum soap but concordant results have not been obtained yet.[3],[4],[5],[10] In fact the properties of aluminum soap depend greatly upon the method of preparation, especially upon whether or not water takes part in the process.[4],[11] Such a fluctuation of the properties can also be considered as an indication of a complicated structure of aluminum soap. Eigenberger[12] proposed aluminum stearate of a polymeric structure. Recently McGee[3] presented a model for the structure of aluminum mono- and di-laurate in which two adjacent alumina octahedra are joined by sharing their edges or corners. Gray and Alexander[4] also reported a linear polymer structure for aluminum soaps, especially for those prepared using aqueous media. Although the opinion somewhat differs in detail from each other, these authors agree at least in adopting the polymeric structure for aluminum soaps, which can also be assumed in the present experiment. It is difficult to determine precisely the molecular structure of aluminum stearate formed in the film, but taking into consideratiou the model presented for aluminum soap by McGee, and Gray and Alexander, it might schematically be depicted as follows.



If this high-molecular structure is allowed for aluminum stearate, the backbone of –Al—O– linkage will lie flat on the surface of water, from which stearyl groups attached to aluminum atom in the backbone will be directed to air. This explains well the experimental results obtained in this work. First, it is expected from this molecular structure of aluminum stearate that the area per stearyl group in this film is larger than the area per stearic acid in the film formed on water containing no metallic ion. Next, since –Al—O– chain is considered flexible, the compressibility of the film should be large compared with that of the film of stearic acid without metallic ion. Further, it may be expected that this film can not resist so large a pressure, as is usually the case with the film of long chain high-molecular substances in which the molecules lie flat on the surface of water.[13] All these presumptions

(8) W. D. Harkins and E. Boyd, *J. Phys. Chem.*, **45**., 20 (1941).
(9) J. W. McBain and W. L. McClatchie, *J. Am. Chem. Soc.*, **54**, 3266 (1932).
(10) Wo. Ostwald and R. Riedel, *Kolloid-Z.*, **69**, 185 (1934); G. H. Smith, H. H. Pomeroy, C. G. McGee and K. J. Mysels, *J. Am. Chem. Soc.*, **70**, 1053 (1948); etc.
(11) T. C. McRoberts and J. H. Schulman, *Nature*, **162**, 101 (1948).
(12) E. Eigenberger and A. Eigenberger-Bittner, *Kolloid-Z.*, **91**, 287 (1940).
(13) W. D. Harkins, E. F. Carman and H. E. Ries, *J. Chem. Phys.*, **3**, 692 (1935).

were proved to be the case by the present experiment.

It is reasonable to assume that the rest of metallic ions of the second group will also form soaps of similar molecular structure as aluminum soap in a certain *p*H range characteristic of each ion. The *p*H value for the maximum of the film expansion seems to depend on the basicity of each ion. It should be emphasized that these metallic ions exhibit a high co-ordination valency and readily form co-ordination compounds with various substances. In presenting a polymer structure of aluminum soap McGee[3] also took the linkage by co-ordination valency into consideration. Presumably all the metallic ions classified into the second group in this experiment will form with stearic acid a soap, complex in structure supported by co-ordination valency. In this point they are different from those classified into the first group, *i. e.*, calcium, barium and magnesium. Now, it is to be noted that all the metallic ions of the second group prove to be either transition elements or elements being trivalent or higher. The ionic radius of these elements is known to be generally small and its ionic potential large, which are considered to be favorable conditions for the formation of complex salts, The fact that metallic ions are also classified largely into two groups similar to those in the present experiment according to the difference in some other surface chemical properties was confirmed by the studies on the effect of metallic ions both on the built-up film of stearic acid carried out by Muramatsu[14] and on the wettability of stearic acid surface carried out by Inaba,[15] both of our laboratory.

Summary

The effect of various metallic ions on the pressure~area curve of the monomolecular film of stearic acid spread on the surface of the solution was studied. It was found that they were classified into two groups; one involves those which make the film condense such as calcium, barium and magnesium and the other those which make it expand such as thorium, aluminum, iron, copper, zinc, mercury, cobalt and nickel. This classification was explained from the standpoint of molecular structure of the resulting metallic soaps. It was suggested that while the soap of the former metals has a simple structure the soap of the latter metals has a complicated polymeric structure. These structures were explained by the characteristic nature of metallic ions of two groups.

The cost of this research has been defrayed from the grant of the Ministry of Education given to one of the authors.

Chemical Institute, Faculty of Science,
Kyūshū University, Fukuoka.

(14) M. Muramatsu and T. Sasaki, in press.
(15) A. Inaba, to be published recently.

Studies on Monomolecular Films. VIII. Rigidity of the Monolayer of Stearic Acid on the Surface of Salt Solutions

By Ryôhei MATUURA

(Received August 2, 1951)

In the preceding paper[1] the effect of metallic ions on the pressure~area curve of the monolayer of stearic acid spread on the surface of the solution was studied. There the metallic ions were classified into two groups, one condensing and the other expanding the film. It was suggested then that the ions of the latter group form, with stearic acid, soaps of a complicated polymeric structure. In order to confirm further this structure the measurement of some rheological properties of the monolayer of stearic acid on the surface of water containing these metallic ions is most desirable.

(1) T. Sasaki and R. Matuura, This Bulletin, **24**, 271 (1951).

In this connection it was found already by Langmuir and Schaefer[2] that the monolayer of stearic acid becomes rigid when it is spread on water containing metallic ions. Blodgett[3] reported that it is difficult to build up the monolayer of stearic acid formed on water containing copper or aluminum ion because of its high rigidity. Rigidity of a film is closely related to the structure of the film, and it is expected that the metallic ions can also be classified with regards to the measurement of the film rigidity into two groups in the same way as in the preceding paper. Therefore, it is attempted in the present experiment to measure the rigidity of the monolayer of stearic acid formed on the surface of water containing various metallic ions and to find how the result can be accounted for by the structure of the film.

Experimental

For the purpose of the present experiment, it is required merely to know the change of the film rigidity due to the presence of various kinds of metallic ions, and so instead of measuring absolute rigidity it was attempted in this experiment to measure simply relative rigidity of the monolayer of stearic acid with or without metallic ions in the substrate by means of a simple device shown in Fig. 1. In this figure a glass thread,

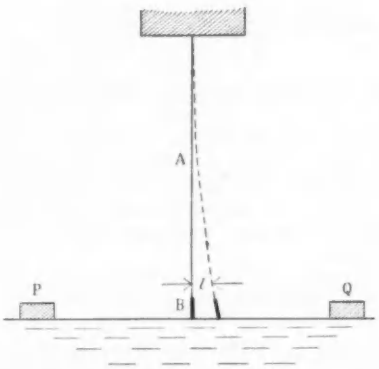


Fig. 1.—Apparatus for measurement of film rigidity.

A, 40 cm. in length and 0.1 mm. in diameter, is suspended vertically over the surface of water in a tray on which the monolayer is to be formed. The top end of the thread is firmly fixed to a suitable support while to the lower end a small platinum wire, B, is welded which is brought to just touching the surface of water. The monolayer was spread on water between two barriers, P and Q, and the film was compressed by moving the barrier P towards the fixed barrier Q. If the monolayer has any appreciable amount of rigidity, the glass thread will be displaced and take a new position as shown by a dotted line in Fig. 1. It took sometimes several minutes or more to reach this equilibrium position. This displacement of the thread, l, which can be taken as a measure of rigidity of the film, was read at every compression by a cathetometer. Surface pressure of the film was simultaneously measured in the same tray using the surface balance already described.[4] The procedure of the preparation of a stearic acid monolayer and the salts used were also the same as before.[1]

Besides the measurement of film rigidity, so-called expansion patterns of the monolayer of stearic acid on the substrate containing metallic ions were investigated as follows, according to somewhat modified method of Schaefer's.[5] The monolayer of stearic acid was prepared on the surface of the solution and a drop of camellia-oil colored red with a dissolved azo dye was placed on it. As the oil spread pushing aside the monolayer of stearic acid, a colored pattern of the various shape was obtained. This pattern, although depending upon the pH value of the substrate, was characteristic of each ion present in the substrate and profoundly affected by the mechanical structure of the monolayer of stearic acid. It was also possible to transfer this pattern from the surface of water to the surface of a filter paper.

Results

It was found that the monolayer of stearic acid formed on the surface of water containing no metallic ion exhibited no rigidity detectable by the present apparatus throughout the whole range of the pH value of the substrate, namely from pH 2 to 10. Likewise, even when calcium, barium, magnesium ion was present in the substrate in the concentration of 10^{-4} mol/l., the monolayer effected so small a displacement of the glass thread even under the high compression that it could hardly be measured accurately.

On the contrary, in the presence of such metallic ions as thorium, aluminum, iron, copper, zinc, mercury, cobalt, nickel, etc. in the substrate the monolayer of stearic acid formed on it revealed a remarkable rigidity which could be measured by a large displacement of the glass thread. In this case the

(2) I. Langmuir and V. J. Schaefer, *J. Am. Chem. Soc.*, **59**, 2400 (1937).
(3) K. B. Blodgett, *J. Am. Chem. Soc.*, **57**, 1007 (1935); *J. Phys. Chem.*, **41**, 975 (1937).
(4) T. Sasaki, *J. Chem. Soc. Japan*, **62**, 796 (1941); R. Matuura and I. Hayasi, *Memoirs of the Faculty of Science, Kyūshū University, Ser. C*, Vol. 1, 31 (1948).
(5) V. J. Schaefer, *J. Phys. Chem.*, **42**, 1089 (1938).

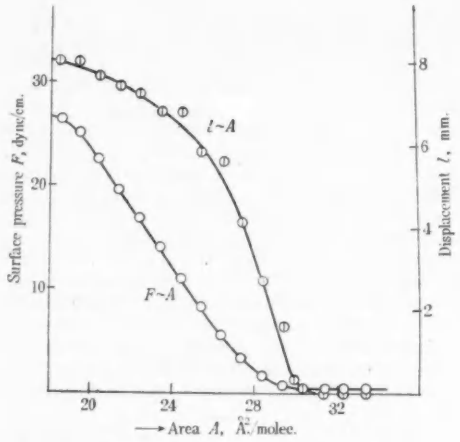


Fig. 2.—Pressure~area and displacement~area curves of the monolayer of stearic acid on water containing aluminum ion.

displacement of the glass thread was intensely dependent upon the degree of compression of the film. The example is shown in Fig. 2 in the case of the substrate containing $AlCl_3$ of 10^{-4} mol/l., and its *p*H being 7.6. In the same figure the pressure~area curve of this film is also depicted for reference. It is noteworthy that the film begins to show a measurable rigidity at neary the same surface area at which the surface pressuse of the film begins to increase perceptibly. Rigidity of the film, then, increases with the increase in the surface pressure until the film collapses at about 25 dynes/cm. Rigidity of the film also depends strongly upon the *p*H value of the substrate. This relation is shown in Fig. 3, where the maximum displacement, *i. e.*, the displacement

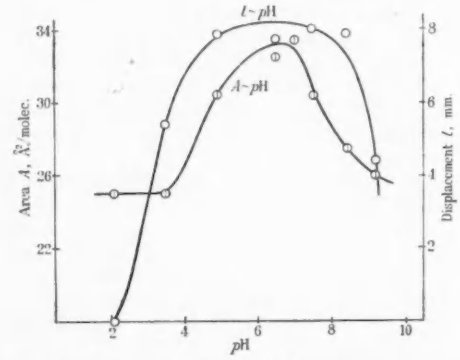


Fig. 3.—Area~*p*H and Displacement~*p*H curves of the monolayer of stearic acid on water containing aluminium ion.

just before the collapse of the film, at each *p*H of the substrate is plotted. In the same figure the area~*p*H curve as shown in Fig. 4 in the preceding paper is also depicted for comparison. It is seen that both the expansion of the film of stearic acid in the presence of aluminum ion and the remarkable rigidity of the film appear in the same range of *p*H of the substrate. Thus in the case of the other metallic ions this relation between expansion and rigidity of the film can also be confirmed similarly by comparing Fig. 4 in this paper with Fig. 4 in the preceding paper.

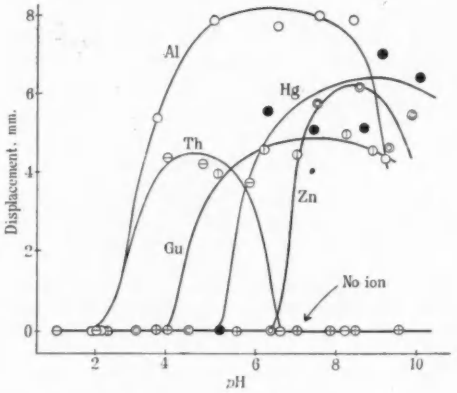


Fig. 4.—Displacement~*p*H curves of the monolayer of stearic acid on water containing some metallic ions.

The expansion pattern is shown schematically in Fig. 5 in the case of the monolayer of stearic acid formed on the surface of water containing calcium, aluminum and thorium ions, together with the pattern obtained in the absence of metallic ions. The surface pressure of the film was kept constant to 10 dynes/cm.

Discussion

The idea of classification of the metallic ions into two groups as proposed in the preceding paper proves to be applicable also to the result of the present experiment. Ions which cause to condense the film of stearic acid make it no rigid, while ions which make the film expand render it remarkably rigid. Thus, rigidity of the film is, probably, another criterion available for the classification of the metallic ions into two groups which are essentially the same as in the former report. The appearance or absence of the remarkable rigidity mentioned above can also be explained

as follows by a simple and complex type of metallic soaps suggested in the preceding paper. That is, the soaps of calcium, barium or magnesium have a rather simple stoichiometric molecular structure, and the molecules of these soaps are likely to be oriented vertically on the surface of water and closely packed. It is expected from this structure of the film that the film has no perceptible rigidity although it may show a fairly small compressibility. On the contrary, the soaps of thorium, aluminum, iron, copper, zinc, mercury, cobalt and nickel were suggested to have a complicated polymeric structure. It is expected in this case that the film will become rigid by interlocking of the long chain. The result of the present experiment shows that this is practically the case. The expansion of the film, its large compressibility, its remarkable rigidity, and the collapse occurring under a rather small surface pressure, all these properties are intimately related to each other and come from the complexity in molecular structure of these metallic soaps. In these properties the monolayer of stearic acid formed on the surface of water containing such metallic ions as thorium, alumlnum, etc. resembles that of proteins well studied by many authors.(6)

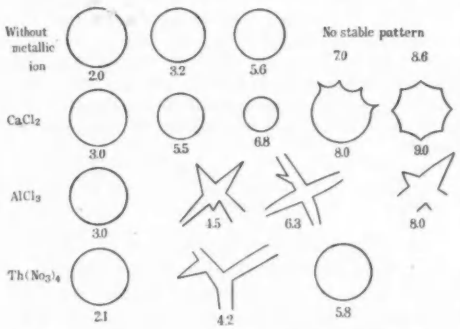


Fig. 5.—Expansion patterns. The numeral for each pattern represents *p*H of the solution.

(6) E. Gorter, *Ann. Rev. Biochem.*, **10**, 619 (1941); H. B. Bull, *Advances in Protein Chemistry*, **3**, 95 (1947); M. Joly, *Research (London)*, Suppl., Surface Chemistry, **1949**, 17.

The experiment on expansion pattern also makes clear the similar difference between the effect of calcium ion and that of aluminum and thorium ions. Indeed in the presence of calcium ion the pattern is somewhat less round than that obtained in the absence of metallic ion, especially at high *p*H, but its irregularity is much less marked compared with the pattern in the presence of aluminum or thorium ion, where the pattern consists mainly of sharp lines. Here the sharpness of the pattern becomes most remakable at a certain *p*H value of the substrate characteristic of each ion. On both sides of this *p*H the pattern gradually loses its sharpness until it becomes perfectly round. Here again the maximum of the sharpness of the pattern corresponds just to the maximum of the film expansion and also to the maximum of the film rigidity.

Summary

A relative rigidity of the monolayer of stearic acid on the surface of water containing various metallic ions was measured by the displacement of the glass thread. It was found, as was pointed out in the preceding paper, that metallic ions were classified largely into two groups, namely ions which render the surface film remarkably rigid and those without such effect. Those of the former group are thorium, aluminum, iron, copper, zinc, mercury, cobalt and nickel, while the latter group involves calcium, barium and magnesium. So-called expansion pattern of the film of stearic acid in the presence of these metallic ions was also studied, the result of which also confirmed this conclusion.

In conclusion, the author thanks to Prof. T. Sasaki for his kind guidance in the course of this study. The cost of this research has been defrayed from the grant of the Ministry of Education given to the professor.

Chemical Institute, Faculty of Science, Kyūshū University, Fukuoka.

Studies on Monomolecular Films. IX. The Effect of Dissolved Dyes on the Monolayer of Stearic Acid

By Ryôhei MATUURA

(Received August 2, 1951)

Introduction

In the preceding two papers[1],[2] the effect of metallic ions on the monolayer of stearic acid was reported. There it was suggested that such metallic ions as thorium, aluminum, iron, copper, zinc, mercury, cobalt and nickel in the substrate formed stearate of a complicated high-molecular structure in the film. It may be expected that some contribution to the confirmation of this suggestion will be obtained by studying the effect of the substance of a large molecule dissolved in the substrate on the monolayer of stearic acid formed on it. For this purpose dyes are considered suitable because the molecules of the dyes are usually large, sometimes forming micelles in a solution, and, in addition, they have one or more ionizable groups which are expected to interact with a polar group of stearic acid. For this reason it has been attempted in this experiment to investigate the interaction between some dyes in the substrate and stearic acid in the film and to compare the result with the effect of such metallic ions as mentioned above. Furthermore, since some dyes are known to be remarkably surface active and their surface chemical properties have been studied in connection with the adsorbed films,[3] foams,[4] etc., it is interesting also for the purpose of studying the surface chemical properties of dyes with regards to their molecular structure to investigate the interaction between dissolved dyes and insoluble films.

Experimental

Dyes used in this experiment were conventionally classified according to their molecular structure into three groups, namely those of acidic, basic and amphoteric ones. As acidic dyes scarlet red and phloxine, as basic dyes chrysoidine, crystal violet and night blue and as amphoteric dyes methyl orange, congo red and trypan red were chosen. Of all these dyes crystal violet, methyl orange and congo red were especially purified by salting out[5] or recrystallization. Comparison of the effect of a commercial dye with that of a purified one on the monolayer of stearic acid gave no essential difference between them, and so the rest of the dyes were used without special purification. Each of these dyes was dissolved in water to the concentration of 10^{-2} mol/l. and aged for about ten days before use. The solution was diluted to 10^{-4} mol/l. when it was used, and the monolayer of stearic acid was spread on the surface of this solution and the pressure~area curve was measured in the same way as described already.[6] The hydrogen ion concentration of the dye solution was varied from 1.5 to 10 using hydrochloric acid and ammonium hydroxide. Here the use of ordinary buffer salts was avoided for controlling *p*H because of the disturbing effect produced by buffer ions as mentioned in the preceding paper.[1] The film experiment was carried out at room temperature.

Results

As to the effect on the stearic acid monolayer, some dyes were remarkable in their action in a *p*H range of the solution proper for each dye, while the effect was imperceptible with other dyes throughout the whole range of *p*H in the present experiment.

(1) **Acidic Dyes.**—Scarlet red showed no effect on the pressure~area relation of the monolayer of stearic acid spread on the surface of the solution throughout the whole range of *p*H, covering from 1.5 to 10, while phloxine modified it considerably in the solution of the acid region. In Fig. 1 the area per molecule of stearic acid at the pressure of 2 dynes/cm. with or without the dyes in the underlying

(1) T. Sasaki and R. Matuura, This Bulletin, **24**, 274 (1951).
(2) R. Matuura, This Bulletin, **24**, 278 (1951).
(3) K. S. G. Doss *Kolloid-Z.* **84**, 138 (1938); **86**, 205 (1939). **87**, 272 (1939).
(4) M. Nakagaki, This Bulletin, **22**, 201 (1949); **23**, 48, 105 (1950).
(5) C. Robinson and H. A. T. Mills, *Proc. Roy. Soc. A*, 131 576 (1931).
(6) T. Sasaki, *J. Chem. Soc. Japan*, **62**, 796 (1941); R. Matuura and I. Hayashi, *Memoirs of the Faculty of Science, Kyushu University, Ser. C*, Vol. 1 (1948).

solution is plotted against its pH. It can be seen that in the presence of phloxine the curve shows a sharp maximum at pH 3.5. It was found that even in the absence of the monolayer of stearic acid the phloxine solution formed rigid adsorbed films of its own at the neighborhood of this pH, and they appear practically insoluble, showing rather a large surface pressure. The question arose that the remarkable expansion of a stearic acid monolayer might come from this adsorbed film of the phloxine solution, but the comparison with the blank experiment showed that it was caused considerably by the interaction between phloxine and stearic acid and could not be explained merely by a simple additive effect of both films.

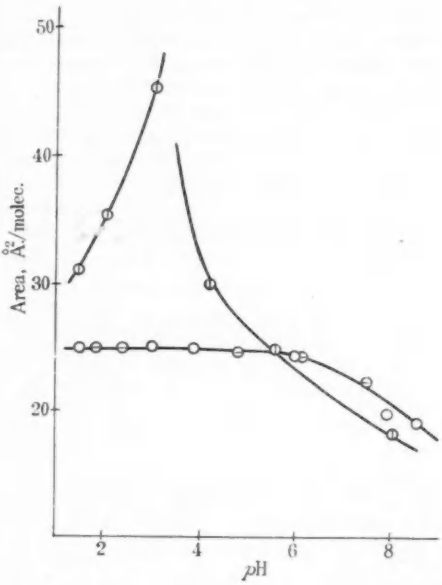


Fig. 1.—Area ~ pH curves of monolayer of stearic acid on water containing acid dyes: ○, without dye; ⊖, scarlet red; ⓘ, phloxine.

(2) Basic Dyes. —Both chrysoidine and crystal violet made the monolayer of stearic acid expand in the solution of the alkaline region as shown in Fig. 2. In the case of night blue the expansion of the monolayer of stearic acid was very remarkable, but this dye formed rigid adsorbed films of its own from especially the alkaline solution, just as phloxine did from the acid solution. The result with night blue is not shown in Fig. 2. A trouble occurred that the solutions of crystal violet and night blue remarkably wetted the paraffined wall of the tray so that the water in the tray overflowed from the edges on compression and the film experiment became impossible. This was largely avoided by using the solution whose concentration was 10^{-5} mol/l. The result with crystal violet shown in Fig. 2 is that obtained using this dilute solution, the film area being that at the surface pressure of 15 dynes/cm. In the case of chrysoidins the concentration of the solution was 10^{-4} mol/l., and the film area

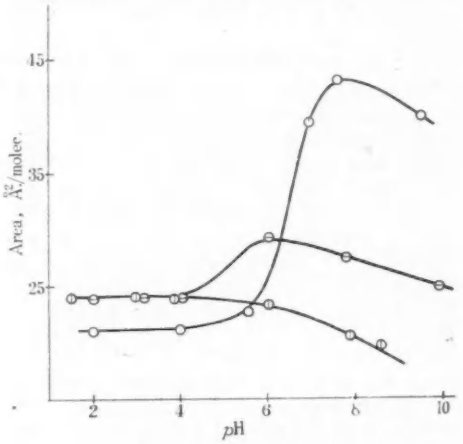


Fig. 2.—Area~pH curves of the monolayer of stearic acid on water containing basic dyes: ○· crystal violet (area at 15 dynes/cm.); ⊖, chrysoidine; ⓘ, without dye.

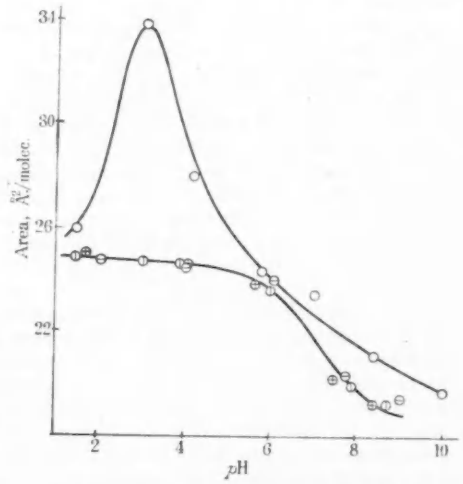


Fig. 3.—Area~pH curves of the monolayer of stearic acid on water containing amphoteric dyes: ○, congo red; ⊕, methyl orange; ⊖, trypan red; ⓘ, without dye.

was that at 2 dynes/cm..

(3) **Amphoteric Dyes.**—It was found that methyl orange and trypan red gave no measurable effect on the monolayer of stearic acid in the *p*H range from 2 to 10, while congo red affected it remarkable when the substrate solution was acidic, as shown in Fig. 3. The film area in Fig. 3 was that at the surface pressure of 2 dynes/cm. It is seen that the curve for congo red shows a maximum at *p*H 3. As the solution becomes more acidic, congo red reduces its solubility and finally precipitates.

Discussion

The result of the present experiment shows that some dyes, when dissolved in the substrate, remarkably expand the monolayer of stearic acid spread on it. It is probable that this comes from the interaction between dyes in the substrate and stearic acid in the film. Here it is of importance to seek for the explanation for this interaction in terms of the molecular structure of the dyes. In the interaction between the dye and stearic acid electric forces due to polar and ionic groups and van der Waals force between nonpolar groups will play an important rôle. Electric forces, of course, are affected by the hydrogen ion concentration of the solution, while van der Waals force is independent of *p*H. Because of the presence of dye ion and stearate ion, both anion, a repulsion will act between the acidic dye and stearic acid in the solution of the alkaline region. This repulsion will disappear in the acid region and the dye will have a possibility of being adsorbed by van der Waals force to the surface of the stearic acid film. This may perhaps be taken as the explanation of the remarkable expansion of the monolayer of stearic acid on the acid solution of phloxine. In the case of scarlet red the ionic repulsion will be much greater because of its strongly ionizable $-SO_3Na$ group and weak van der Waals attraction due to a small size of the molecule. This leads to the failure in adsorption to the monolayer of stearic acid throughout the whole range of *p*H in the present experiment. The remarkable expansion of the monolayer of stearic acid in the presence of congo red at *p*H 3 may also be explained by van der Waals adsorption of the dye to the monolayer. That is, at this *p*H, being the isoelectric point of congo red, the electric repulsion will be the least between the dye and stearic acid due to the lack of the electric charge as a whole, and the van der Walls force will become the dominant one. In case of trypan red, although the molecule is large, five sulfonic groups will act to shift its isoelectric point towards more acidic side, which prevents the adsorption from taking place. It might be expected that here the adsorption by the van der Waals force will occur if the solution is rendered much more acidic than that in the present experiment.

The situation is different in the case of basic dyes. They produce dye cations which are, presumably, capable of combining with stearic acid to form stearates. The degree of ionization of the basic dye becomes larger while that of stearic acid becomes smaller as *p*H of the solution decreases, and, consequently, it is expected that the adsorption becomes most pronounced at a certain *p*H value of the solution. This is confirmed by the present experiment, as shown in Fig. 2, where it is seen that the maximum expansion of the stearic acid monolayer occurs at *p*H 6 in the case of chrysoidine and at *p*H 7.8 in the case of crystal violet. In order to know further the significance of ionic interaction between basic dyes and stearic acid, the effect of crystal violet on the monolayer of cetyl alcohol was investigated. The condition of the experiment was the same as in the case of the monolayer of stearic acid. The result is shown as area~*p*H curves in Fig. 4. It should be noted that the expansion of the monolayer of cetyl alcohol is much smaller

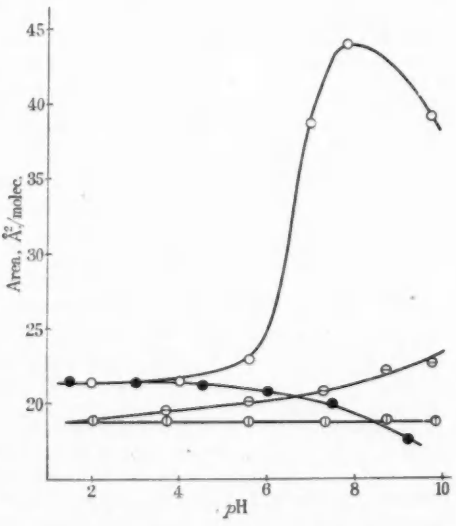


Fig. 4.—Comparison of the effect of crystal violet on the film area (at 15 dynes/cm) of stearic acid with that of cetyl alcohol: ○, stearic acid with dye; ●, stearic acid without dye; ⊖, cetyl alcohol with dye; ⓘ, cetyl alcohol without dye.

than that of stearic acid in the presence of crystal violet. This is explained by the fact that cetyl alcohol is much less ionizable than stearic acid and so ionic interaction, a chief factor of the mutual interaction considered above, is much weaker between cetyl alcohol and crystal violet than between stearic acid and crystal violet. Such an ionic interaction has also been confirmed in the case of proteins and some dyes.[7]

It should be emphasized here that the mechanism of the interaction between dyes and stearic acid is fairly complex in nature, involving at least the ionic interaction and van der Waals force. The latter is also considered as a main factor determining the solubilization of dyes by detergents, the phenomenon which became to draw attention of many investigators recently.[8] The author reported in the preceding paper the special interaction between stearic acid and such metallic ions as aluminum, thorium, etc. Comparing this with that between stearic acid and dyes studied in the present experiment we can find some similarities as well as differences in the mechanism underlying them. It may be mentioned that the basic dyes react with stearic acid in a similar manner as thorium and aluminum ions do with stearic acid as far as the expansion and the complex structure of the resulting film are concerned. This view can also be confirmed by the experiment of wettability carried out by Inaba[9] of our laboratory.

(7) I. M. Klotz and F. M. Walker, *J. Am. Chem. Soc.*, **69**, 1609 (1947).
(8) H. B. Klevens, *Chem. Revs.*, **47**, 1 (1950).

Summary

The interaction between the dyes dissolved in water and the monolayer of stearic acid spread on it was studied and discussed. It was shown that a remarkable expansion of the monolayer of stearic acid in the presence of phloxine and congo red was explained chiefly by the van der Waals adsorption, while that in the presence of basic dyes was explained chiefly by the ionic interaction. It was suggested that the interaction between basic dyes and stearic acid was analogous in some respects to the formation of soaps of such metals as thorium, aluminum, etc.

In conclusion the author expresses his hearty thanks to Prof. T. Sasaki for his kind guidance in the course of this study. The cost of this research has been defrayed from the grant of the Ministry of Education given to the professor.

Chemical Institute, Faculty of Science, Kyūshū University, Fukuoka.

(9) A. Inaba, to be published recently.

On Some Dark-colored Chloroplumbates (II, IV) of the Type $[M^{III}A_6]PbCl_6$

By Masayasu MORI[1]

(Received September 6, 1951)

Introduction

In 1934 Norman Elliott[2] determined the magnetic susceptibility of a violet black compound, $(NH_4)_2SbBr_6$, which had for years been generally believed to be a quadrivalent antimony compound, and found that the substance was diamagnetic and therefore could not contain quadrivalent antimony in an ordinary sense. Three years later K. A. Jensen[3] analysed the crystal structure of three similar compounds, $(NH_4)_2SbBr_6$, Rb_2SbBr_6 and Rb_2SbCl_6, by the x-ray powder method and found scarcely any difference between the lattice structure of these compounds and that of ammonium hexabromostannate (IV) etc. except

(1) The present address: The Institute of Polytechnics Osaka City University, Minami-Ogi-Machi, Kitaku, Osaka.
(2) N. Elliott, *J. Chem., Phys.*, **2**, 298 (1934).
(3) K. A. Jensen, *Z.anorg. Chem.*, **232**, 193 (1937); *ibid.*, **233**, 295 (1937).

in their lattice dimensions, six halogen atoms being arranged around one antimony atom to make an octahedral structure. It is thus probable that these octahedral ions $SbBr_6$ are a mixture of $Sb\,Br^{-3}{}_6$ (in which Sb is tervalent) and $Sb\,Br^{-}{}_6$ (in which Sb is quinquevalent).

Yet another problem remains unsolved: Why do these antimony compounds present a dark violet appearance, which neither tervalent nor quinquevalent antimony compounds do?

While attempting to get some double salts between cobalt(III) or chromium(III) ammine chlorides and chlorides of heavy metals, the present author obtained crystalline compounds of empirical formulas, $[Co(NH_3)_6]PbCl_6$ (violet black), $[Co(NH_3)_5H_2O]PbCl_6$ (puce-colored), $[Cr(NH_3)_6]PbCl_6$ (violet black) and $[Cr(NH_3)_5H_2O]Pb\,Cl_6$ (puce-colored). These compounds, which from their formulas alone might be supposed to have tervalent lead atoms, have shown several points of resemblance to the antimony compounds above mentioned,—for example, in their anomalous coloration and magnetic property. In this paper the methods of preparation and magnetic data pertaining to these compounds will be given.

Experimental

Preparation of Chloroplumbates of the Type $[M^{III}A_6]PbCl_6$.—A solution containing chloroplumbic (IV) acid should first be prepared:

Three and three tenth grams of lead nitrate and 1 g. of potassium chlorate are dissolved in 50 ml. of water and the solution is poured little by little into 50 ml. of concentrated hydrochloric acid containing 1 g. of potassium chlorite. The white precipitate of lead(II) chloride produced at each addition is brought into solution by shaking and mixing, before the next portion is added. The yellow solution thus produced will contain lead(IV) at about 0.1 *M* in concentration.

In order to prepare a chloroplumbate of the type $[M^{III}A_6]PbCl_6$ (where M=Co or Cr), a solution of chloroplumbic acid thus prepared is mixed with a solution of a metal ammine, $[M^{III}A_6]Cl_3$; and the mixture is digested for some time. As starting metal ammine salts, it is recommended that those complex salts should be employed the preparation of which is the easiest. These metal ammines, together with proper solvents and modes of digestion, are given in Table 1.

In each case of preparation a chloroplumbate (IV) of a sallow color is first formed, and this, with liberation of chlorine, is quickly changed into a dark-colored chloroplumbate of the type $[M^{III}A_6]PbCl_6$. It is filtered, and washed with dilute hydrochloric acid and alcohol.

These dark-colored chloroplumbates are hardly soluble in dilute hydrochloric acid but are decomposed by water forming a suspension of lead dioxide. When any of these compounds is warmed with dilute sulfuric acid and iron(II) sulfate, all the lead is precipitated as lead(II) sulfate, and the supernatant liquid shows the color of the complex ions employed as the cation source.

Table 1

Salts to be prepared	Starting metal ammines	Dissolved in	Mixed with H_2PbCl_6 aq. and digested
$Co(NH_3)_6$–$PbCl_6$	4 g. of $Co(NH_3)_6Cl_3$[4]	300 ml. of 3*N* HCl	at 60°C. for 20 min.
$Co(NH_3)_6$ H_2O–$PbCl_6$	5 g. of $Co(NH_3)_5H_2O$–oxalate[5]	100 ml. of *N*/2 HCl	at 40°C. for 5 min.
$Cr(NH_3)_6$–$PbCl_6$	5 g. of $Cr(NH_3)_6$–$(NO_3)_3$	300 ml. of 3*N* HCl	at 60°C. for 20 min.
$Cr(NH_3)_5$ H_2O–$PbCl_6$	5 g. of $Cr(NH_3)_5H_2O$–$(NO_3)_3$	100 ml. of *N* HCl	at 40°C. for 5 min.

Of the starting complex salts mentioned above, hexamminechromium(III) nitrate has been prepared by a method modified from one proposed by S. M. Jörgensen, and aquopentamminechromium(III) nitrate by a new method of the present author's, which will be published shortly.

Analyses:

Calcd. for $Co(NH_3)_6PbCl_6$ or $[Co(NH_3)_6]_2(Pb^{II}Cl_6)$-$(Pb^{IV}Cl_6)$: Pb(total), 35.64 %; Pb(IV), 17.82 %; Co, 10.14 %; Cl, 36.63 %. Found: Pb(total), 35.89 %: Pb(IV) (determined by iodometry), 17.96 %; Co, 9.76 %; Cl, 36.95 %.

Calcd. for $Co(NH_3)_5H_2OPbCl_6$ or $[Co(NH_3)_5H_2O]_2$-$(Pb^{II}Cl_6)(Pb^{IV}Cl_6)$: Pb(total), 35.60 %; Pb(IV), 17.80 %; Co, 10.13 %; Cl, 36.56 %. Found: Pb (total), 35.88 %; Pb (IV), 16.85 %; Co, 9.62 %; Cl, 36.59 %.

Calcd. for $Cr(NH_3)_6PbCl_6$: Pb(total), 36.09 %; Cr, 9.06 %; Cl, 37.05 %. Found: Pb, 36.00 ; Cr, 8.63 %; Cl, 37.46 %.

Calcd. for $Cr(NH_3)_5H_2OPbCl_6$: Pb (total), 36.05 %; Cr, 9.04%; Cl, 37.00 %. Found: Pb, 35.00%; Cr, 9.30 %; Cl, 37.64 %.

Magnetic Susceptibility of the Chloroplumbates of the Type $[M^{III}A_6]PbCl_6$.—In order to test whether the Pb's in such cobalt complex chloroplumbates as $[Co(NH_3)_6]PbCl_6$ have unpaired electrons or not, it is only necessary to determine their magnetic susceptibility; for, in the tervalent cobaltammine complex ions the electrons are known to be all paired.

Measurements by the Gouy's cylinder method have given, as the mass-susceptibility of $[Co(NH_3)_6]$-$PbCl_6$ and $[Co(NH_3)_5H_2O]PbCl_6$, values in the neighborhood of -0.3×10^{-6} E. M. U., thus proving that the Pb's in these compounds have no

(4) Hexamminecobalt(III) chloride is easily prepared by bubbling air through a solution of cobalt (II) chloride in aqueous ammonia in the presence of ammonium chloride and adsorption charcoal. J. Bjerrum, "Metal Ammine Formation in Aqueous Solutions," P. Haase and Son, Copenhagen, 1941. See *Chem. Abst.*, **34**, 6534 (1941) and also W. C. Fernelius *et al.*, "Inorganic Syntheses" Vol. II, McGraw Hill Book Co., New York, N. Y., 1946, p. 216.

(5) S. M. Jörgensen, *J. Prak. Chem.*, **31** 89 (1985); *Z. anorg. Chem.*, **17**, 461 (1898).

unpaired electrons and therefore cannot be tervalent in an ordinary sense.

The corresponding chromium compounds have shown strong paramagnetism, but this may be due to the presence of unpaired electrons in tervalent chromium complex ions. Considering every point of resemblance between these cobalt (III) and chromium(III) ammine chloroplumbates, it seems quite reasonable to think that in the latter, too, the Pb's do not exist in the tervalent state.

It therefore seems adequate to name these compounds as hexamminecobalt(III) chloroplumbate (II, IV) etc.

Considerations

Several series of compounds are known which have a characteristic dark color and contain the same element in different valence states.[6] The chloroplumbates (II, IV) described above appear to be new additions to these series, because:

(i) They are all dark colored which is inexplicable from the colors of the component ions. (Double salts between $[Co(NH_3)_6]Cl_3$ etc. and $PbCl_2$ show the color of $Co(NH_3)_6^{+++}$ ions etc.[7] and so do the chloroplumbates (IV) of these complex cations.)

(ii) The magnetic property of $[Co(NH_3)_6]PbCl_6$ and $[Co(NH_3)_5H_2O]PbCl_6$ denies the existence of any unpaired electrons in Pb's; and it is natural to think that the compounds contain $Pb\,Cl^{-4}{}_6$ and $PbCl^{-2}{}_6$.

(iii) Two very similar series:

$$(NH_4)_2SnBr_6,\ (NH_4)_2SbBr_6,\ (NH_4)_2TeBr_6$$

and

$$[Co(NH_3)_6]TlCl_6,\ [Co(NH_3)_6]PbCl_6,$$
$$[Co(NH_3)_6]BiCl_6$$

are obtained where Sn, Sb and Te as well as Tl, Pb and Bi are arranged in the order of atomic numbers.[8]

Some hypotheses have been advanced by different authors as to the reason of the coloration of these mixed valence compounds ("Oscillieren" or "resonance" for example); but the experimental evidence is not sufficient for any of them; and anything like a perfect solution of the problem must depend on the fruits of further researches.

Summary

(1) Compounds ranging from violet black to puce in color, $[Co(NH_3)_6]PbCl_6$, $[Cr(NH_3)_6]PbCl_6$, $[Co(NH_3)_5H_2O]PbCl_6$ and $[Cr(NH_3)_5H_2O]PbCl_6$ have been prepared, by mixing a solution of $[Co(NH_3)_6]Cl_3$ etc. (in dil. HCl) and a solution containing H_2PbCl_6 and digesting them at 40° to 60°.

(2) $[Co(NH_3)_6]PbCl_6$ and $[Co(NH_3)_5H_2O]PbCl_6$ are diamagnetic and therefore it seems natural to consider these compounds as hexamminecobalt(III) chloroplumbate (II, IV) and aquopentamminecobalt(III) chloroplumbate (II, IV) respectively.

It is the author's genuine pleasure to acknowledge his indebtedness to Mr. Meitaro Endo without whose wholehearted coöperation in magnetic measurements, these pages could never have been written.

His sincere thanks are also due to Prof. Kenjiro Kimura and Dr. Yukio Murakami of the University of Tokyo for their tutorial advice and offer of laboratory facilities.

Chemical Institute, Faculty of Science, The University of Tokyo, Tokyo

(6) L. Pauling, *Chem. Eng. News*, **25**, 2970 (1947).

(7) F. Ephraim and P. Mosimann, *Helv. Chim. Acta*, **6**, 1122 (1923); *ibid.*, **9**, 630 (1926).

(8) In a letter to the author, Prof. Tokunosuké Watanabé and Mr. Masao Atoji of the University of Osaka have kindly informed him that the crystal lattice structure of $Co(NH_3)_6PbCl_6$ or $[Co(NH_3)_6](Pb^{II}Cl_6)(Pb^{IV}Cl_6)$ exhibits a close resemblance with a slight deformation to that of $Co(NH_3)_6TlCl_6$, the latter being composed of $Co(NH_3)_6^{+3}$ and $TlCl_6^{-3}$ arranged in a NaCl-type. See *Acta Cryst.*, **3**, 405 (1950).

Additions and Corrections

Volume 23, 1950

Contents of Volume 23, 1950.
Page Ⅳ. In line 39, for "Le pléochroïsme" read "Le dichroïsme".

S. Miyakawa, K. Haségawa et T. Uémura. Le dichroïsme de la molecule des matieres colorantes dans l'alcool polyvinylique.
Page 260. In col. 1, line 7 from the end, for "coéfficient" read "coefficient". In col. 2, line 21, for "X et Q" read "X et Y".

Author Index to Volume 23, 1950.
Page 264. In col. 1, line 12, for "pléochroïsme" read "dichroïsme".

Volume 24, 1951

S. Miyakawa et T. Uémura. Etudes spectroscopiques des complexes métalliques du diphénylthiocarbazone. II.
Page 27. In col. 2, text line 3, for "pent" read "peut".

Y. Urushibara, M. Chuman and S. Wada. A New Synthesis of Progesterone.
Page 83. In col. 2, line 6, "ot" should read "to". In formula (III), for "Pregenone oxide acetate" read "Pregnenolone oxide acetate". In formula (V), for "Allopregnane-triol-(3β, 2α, 20)" read "Allopregnane-triol-(3β, 5α, 20)". In formula (VI), for "5α-Hydroxy-allopregnanane-dione-(3,20)" read "5α-Hydroxy-allopregnane-dione-(3,20)".

S. Okajima and Y. Kobayashi. Plastic Deformation of the Regenerated Cellulose Fibers. I and II.
Page 88. In col. 1, line 7, for "out" read ", but".
Page 89. In Fig. 7, for "No. 60" read "No. 6a".
Page 91. In col. 1, line 11 from the end, for "streching" read "stretching". In col. 1, line 5 from the end, for "dry state 0 and 1." read "dry state 0 and 1,".

K. Sugino and Eiichi Inoue. Synthesis of Some Organic Compounds by Electric Discharge. I-V.
Page 95. In Table 1, line of Temp. of ozonizer, col. of Run 2, for "50" read "65", and in the same table, the same line, but col. of Run 3, for "50" read "70". In col. 2, text line 14, the first word "to" should be removed.
Page 96. In Table 2, line of Method of cooling of the mixed gas, col. of Run 3, for "Fig. 3" read "Fig. 2". In col. 2, line 14, for "prat" read "part". In Table 3, line of Effective length, col. of Run 4, for "70" read "75".
Page 97. In col. 1, line 6, for "13–20," read "13–20 %". In Table 6, line of Primary kwhr., col. of Run 3, for "1.35" read "1.36". In Table 6, line of Air, col. of Run 2, "31.1" read "93.1". In Table 6, line of Adipic acid, col. of Run 2 for "(26 %)" read "(25 %)". In Table 6, line of Adipic acid, col. of Run 3, for "(13 %)" read "(3 %)". In Table 6, line of Distillation residue, col. of Run 2, for "(25 %)" read "(26 %)".

T. Ikeda. A Note on the Theory of Solution of Hydrated Systems.
Page 101. In col. 2, line 16 (Eq. (2)), for "V_+" read "ν_+" and for "V_-" read "ν_-".
Page 102. In Table 1, line 26 (Note•), for "α^-" read "α_-". In col. 1, foot-note (2), for "*ibid*" read "*J. Am. Chem. Soc.*"
Page 103. In col. 1, line 5, for "a_-" read "α_-". In col. 2, line 30, "and 22 La^{+++}" should read "and 22 for La^{+++}".
Page 104. In Table 4, line of Glycerol, col. of No. of free OH radicals, for "2" read "3".

Y. Yasumori. Amperometric Titration of Potassium with Sodium Dipicrylaminate.
Page 110. In col. 2, line 9, "negleting" should read "neglecting".

E. Mizuki and S. Fujisawa. Phenomenological Theory of Intermediate Intensity Reciprocity-Law Failure at and near the Optimum in Photographic Exposure.
Page 111. In col. 1, line 1, for "inonic" read "ionic".
Page 113. In col. 1, last line of foot-note (8), for "schieved" read "achieved".
Page 114. In col. 2, line 12, for "redresenting" read "representing".
Page 115. In col. 2, lines 4 and 10, for "descend" read "descent".

S. Hakomori and S. Tamura. The Presence of Bismuth in Fish Bones and Human Teeth as Revealed by Cathodo-luminescence Method of Analysis.
Page 117. In col. 2, line 29, for "the boes of" read "the bones of". In col. 2, line 10 from the end, the last word "indis" should read "indis-".

S. Yamaguchi. On the Etched Surfaces of Nickel Single Crystals Revealed by Means of Electron Diffraction and Microscopy.
Page 123. In col. 2, line 20 from the end, for "speccimen" read "specimen".

S. Yamada. Researches on Dichroism of Planer Complex. III.
Page 127. In col. 2, line 12, the first word "ween" should be "tween".

S. Miyakawa, I. Tanaka et T. Uémura. Etudes spectrochimiques due cyclooctatétraène (C_8H_8) et du $C_{16}H_{16}$.
Page 136. In col. 1, text line 2, the last word "intére-" should be "intéres-", and in col. 1, text line 3, the first word "ssante" should be "sante".

Page 137. In col. 1, text line 13, for "représenté" read "représentée".
Page 140. In col. 1, line 4, for "considerant" read "considérant".

Y. Matsushima. Studies on Amino-hexose. II.

Page 145. In col. 2, line 23, for "RCOCl $\xrightarrow{C_2HNH_2}$" read "RCOCl $\xrightarrow{CH_2N_2}$".

S. Kawasumi. Equilibrium of the CO_2-NH_3-Urea-H_2O System under High Temperature and Pressure. I.
Page 150. In col. 2, line 20, "etm" should read "tem".

K. Tamaru. Pyrolysis and Combustion of Cellulose in the Presence of Inorganic Salts.
Page 167. In col. 1, line 14 from the end, for "fire-roofing" read "fire-proofing". In col. 1, line 13 from the end, for "valume" read "volume". In col. 2, text line 1, for "conbustible" read "combustible".

K. Tamaru. On the Action of Carriers in the Catalytic Hydrogenation of Acetylene by Palladium Catalyst.
Page 178. In Fig. 3, the author writes the arrows such as "↙↙" instead of "↙↙".

H. Honda and K. Ouchi. Magnetic Properties of Condensed Aromatic Hydrocarbons with Four Benzene Nuclei. I.
Page 182. In Eq. (5) (determinant), "ε_2" should be added in col. 9, line 4.

K. Matsuzaki and H. Sobue. Heterogeneous Hydrolytic Degradation of Cellulose.
Page 184. In col. 2 line 6, for "heir" read "their".